

# SILVER(I) OXOANION EQUILIBRIA IN MOLTEN ALKALI NITRATES



GÖRAN THOMÉ

Lund 1980



SILVER(I) OXOANION EQUILIBRIA IN MOLTEN  
ALKALI NITRATES

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| Title and subtitle<br>Silver(I) Oxoanion Equilibria in Molten Alkali Nitrates                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |                         |                                        |  |
| <p><b>Abstract</b><br/>         The <u>complex formation</u> between <u>silver(I)</u> and the <u>oxoanions</u> <math>\text{NO}_2^-</math>, <math>\text{IO}_3^-</math>, <math>\text{CrO}_4^{2-}</math>, <math>\text{MoO}_4^{2-}</math> and <math>\text{PO}_4^{3-}</math> in <u>molten</u> equimolar <math>(\text{K}, \text{Na})\text{NO}_3</math> has been studied mainly by <u>emf</u> and <u>solubility</u> measurements. Stepwise formation of complexes has been considered and 1:1, 1:2 and 2:1 complexes between Ag(I) and the oxoanions, <math>\text{Ox}^{q-}</math>, have been detected in most cases. The study has been performed in a <u>temperature</u> interval from 523 K to 623 K in order to evaluate <math>\Delta H_1^0</math> and <math>\Delta S_1^0</math> for the process <math>\text{Ag}^+ + \text{Ox}^{q-} \rightarrow \text{AgOx}^{(q-1)-}</math>. <math>\Delta S_1^0</math> is in the range 20-30 <math>\text{Jmol}^{-1}\text{K}^{-1}</math> for all the oxoanions (except <math>\text{NO}_2^-</math>, see below) while <math>-\Delta H_1^0</math> increases with increasing negative charge of the oxoanions. From the <math>\Delta H_1^0</math> values and the sizes of the cations it is concluded that bonds of considerable covalent character are formed between Ag(I) and the oxoligands. The nitrite complex formation displays a larger value of <math>-\Delta H_1^0</math> than expected for coordination via oxygen and <math>\Delta S_1^0</math> is <math>-15\text{Jmol}^{-1}\text{K}^{-1}</math>. Nitrogen coordination is suggested as an explanation. The complexation has been studied by solubility methods at one temperature, 553 K, for the <math>\text{IO}_3^-</math>, <math>\text{CrO}_4^{2-}</math>, <math>\text{MoO}_4^{2-}</math> and <math>\text{PO}_4^{3-}</math> systems.</p> <p><u>Solid solutions</u> of sodium oxoanion salts in the corresponding silver salts have been discovered and the activities of the components have been evaluated and related to ideal Temkin activities and to the regular solution model. <u>Phase transitions</u> in the solids have been detected and studied by thermodynamic and X-ray methods.</p> |                         |                                        |  |
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This review gives a summary of results which have been communicated in the following papers. They will be referred to by their Roman numerals.

- I      B. Holmberg and G. Thomé  
Nitrite Complexes of Silver(I) in Molten Alkali Nitrates.  
Inorg.Chem. In press.
- II     B. Holmberg and G. Thomé  
Thermodynamics of Solid Solutions  $(\text{Ag,Na})\text{IO}_3$  and Silver Iodate  
Complexation in Molten  $(\text{K,Na})\text{NO}_3$ . A Potentiometric and Solubility  
Study.  
Submitted for publication.
- III    B. Holmberg and G. Thomé  
Solid Solutions  $(\text{Ag,Na})_2\text{CrO}_4$  and Silver Chromate Complexes in  
 $(\text{K,Na})\text{NO}_3$  Melts. A Potentiometric, Spectrophotometric and Solubility  
Study.  
Submitted for publication.
- IV    B. Holmberg and G. Thomé  
Thermodynamics of Solid Solution  $(\text{Ag,Na})_2\text{MoO}_4$  and Silver Molybdate  
Complexation in Molten  $(\text{K,Na})\text{NO}_3$ . A Potentiometric and Solubility Study.  
Submitted for publication.
- V      B. Holmberg and G. Thomé  
Complex Formation between  $\text{Ag}^+$  and  $\text{PO}_4^{3-}$  in Molten Equimolar  
 $(\text{K,Na})\text{NO}_3$ . A Comparison with Other Silver(I) Oxoanion Complexes  
in the same Medium.  
Submitted for publication.

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## INTRODUCTION

Although many applications of molten salts have been found and much research has been performed during the last twenty years there is a great need for experimental data in this field of chemistry. The present state of molten salt chemistry can be judged from several monographies.<sup>1-8</sup>

Industrial applications in fields such as heat transfer, electrowinning of metals, glass manufacture and catalysis are well-known and others, e.g. fuel cells, thermal storage, solvent extraction and chromatography have been proposed.<sup>9</sup> Ionic melts are available in a wide temperature range and the low vapour pressure allows them to be used at normal pressures without serious loss of salt. The high electrical conductivity, good heat transfer properties and the ability to dissolve metals, oxides, carbides, nitrides and other salts are of importance for technical use of molten salts. Furthermore their wide potential span between the decomposition limits makes them suitable solvents for electrochemical processes. Much of the fundamental chemistry is, however, still unknown and there is a growing interest for research in this field of chemistry.

The properties of a melt depend on the species it is constituted from and the formation of complex ions in a melt has generally been found to be of great importance in determining the physiochemical properties of the systems. Complex formation studies, aiming at an increased knowledge of structure and energetics in simple model systems, are therefore of importance for the building up of general theories and models of molten salt systems.

Metal halide complexation in molten alkali nitrates has been thoroughly investigated at this laboratory prior to the present work. Silver bromide and iodide complexation has been treated in a number of papers.<sup>10-12</sup> Cobalt halide complexes have been studied by spectrophotometry.<sup>13</sup>

Alkali nitrates are readily available in pure form at a low cost. They have low melting points which can be reduced by using eutectic mixtures. Eutectic (K,Na)NO<sub>3</sub> melts already at 222°C which should be compared to 307°C for NaNO<sub>3</sub> and 334°C for KNO<sub>3</sub>. The thermal stability is good at lower temperatures while nitrates decompose to nitrite and oxygen above 400°C. The melts have pronounced ionic character and nitrate ions are expected to form comparably weak complexes with most metal ions. On the other hand alkali ni-

trates are not the simplest kind of ionic liquids because of the polyatomic nitrate ion. The nitrate ion, furthermore, can be involved in Lux-Flood acid-base reactions<sup>14</sup> as an oxide ion donor, i.e. a Lux-Flood base.

The classification of acceptors and donors in terms of (a)- and (b)-behaviour (or "hard" and "soft") has been proven to be a useful rationalization of a large amount of thermodynamic data on stabilities of complexes in aqueous solution and various organic solvents.<sup>15-18</sup>

An analysis of  $\Delta G_j^0$  for the process  $M + jL \rightarrow ML_j$  in terms of enthalpy and entropy changes according to

$$-\Delta G^0 = -\Delta H + T\Delta S^0 \quad (1)$$

reveals quite different  $\Delta H^0 - \Delta S^0$ -patterns for (a)-(a)-systems as compared to (b)-(b)-systems. The general pattern has been interpreted as follows.<sup>19</sup>

The formation of an (a)-(a) complex is associated with breaking of strong bonds between donor and acceptor ions on the one hand and solvent molecules on the other. The predominantly ionic donor-acceptor bond does not fully compensate for the desolvation energy required. However, the configurational entropy of the solution is increased by the liberation of solvent molecules, which gives a favourable  $T\Delta S^0$  contribution to  $\Delta G^0$ . The general pattern can thus be summarized  $\Delta H^0 \gtrsim 0$  and  $\Delta S^0 > 0$ .

For a typical (b)-(b)-interaction the situation is about the opposite one. The donor-acceptor bond is thought to be predominantly covalent and the coordinate bond formation is associated with a considerable evolution of heat. On the other hand, the constituent ions are poorly solvated and the complexation is therefore associated with small or, in most cases, even negative  $\Delta S^0$ . The general pattern is  $\Delta H^0 < 0$  and  $\Delta S^0 \lesssim 0$ .

In molten alkali nitrates most studies of complex association have concerned typical (b)-(b)-systems, and the classification from aqueous solution has appeared to hold. In a typical (a)-(a)-system the stability of the complexes in molecular solvents is thought to be due to entropy gains predominantly from desolvation of the central ion (and sometimes from the ligand ion, when this is strongly solvated, as in the case of  $F^-$  in aqueous solution) when the complex is formed. Obviously the model used in the case of ordinary room temperature solvents - where the complexes owe their stability to a gain in entropy - does not work in an ionic solvent,

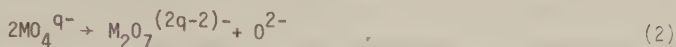
characterized by an inherent short range order around both solute and solvent ions. One might expect entropy changes due to changes in internal degrees of freedom for polyatomic ligands and solvent anions to be of an order of magnitude quite comparable to the rather small configurational entropy changes inferable from the general structural characteristics of ionic melts.

In this work interactions between a typical (b)-acceptor, Ag(I), and a number of oxoanions, expected to act as weak or potential class (a) donors, are studied. The silver(I) ion is a suitable probe ion for a comparative study of complexation of various potential ligands, since changes in  $\text{Ag}^+$  activity are easily followed in a large concentration range by potentiometric methods in nitrate melts.<sup>20</sup> The purpose has been to elucidate what complexes are formed in each oxoanion system, to determine the stability of the complexes and, by variation of the temperature, to estimate  $\Delta H^0$  and  $\Delta S^0$  for the complex formation process. Furthermore, effects of variations in ionic charge, size and chemical character of the central ion in the oxoanion on the thermodynamic parameters characterizing the complexation should be revealed and related to current theories on pair association in ionic liquids and Lewis basicity of oxo-systems.

The selection of oxoanions is limited by factors such as the applicability of available measuring techniques and the stability of the oxoanions and oxoanion salts at the elevated temperatures of the melts. It was considered to be of special importance to study effects of charge differences. The choice of ligands is summarized in Table 1.

The univalent ions are of certain interest since they give no charge asymmetry in the melt that might be the origin of configurational changes upon complexation and hence no such structural contributions to the entropy of the complexation are expected. The only information obtained so far about silver(I) complexation with polyatomic ions of this kind is from the cyanide system.<sup>21</sup> Halate ions are in general not stable in nitrate melts since they decompose under liberation of oxygen. Iodate, however, is the most stable of these ions and it is not reduced under the conditions of this study.<sup>11</sup> Formation of nitrite in molten  $\text{KNO}_3$  was early detected<sup>22</sup> and the influence of the nitrite ion on the complexation of Ag(I) in alkali nitrate melts is of general interest because of the spontaneous formation of  $\text{NO}_2^-$  in minor concentrations in these melts.<sup>23</sup>

## Condensation reactions of acid-base type



are likely to occur, judging from the aqueous chemistry of  $\text{CrO}_4^{2-}$ ,  $\text{MoO}_4^{2-}$ ,  $\text{WO}_4^{2-}$  and  $\text{PO}_4^{3-}$ . Equilibrium constants for reaction (2) have been determined for  $\text{CrO}_4^{2-}$ ,  $\text{MoO}_4^{2-}$  and  $\text{WO}_4^{2-}$ .<sup>24</sup> For  $\text{CrO}_4^{2-}$  and  $\text{MoO}_4^{2-}$  negligible amounts of dimer are formed in the pure  $(\text{K},\text{Na})\text{NO}_3$  solvent in the concentration range suitable for studies of complexation with cations. A thorough investigation of the depolymerization of condensed phosphates in nitrate melts by Copeland and coworkers<sup>25,26</sup> and a low equilibrium constant for the dimerization of  $\text{PO}_4^{3-}$  in pure  $\text{KNO}_3$  at 350 °C reported by Shams el Din and Gerges<sup>27</sup> together with analyses of silver-containing melts in this study confirm the stability of  $\text{PO}_4^{3-}$ .<sup>V</sup>

Chromate and molybdate complexes in different alkali nitrate solvents have recently been investigated by Sachetto and coworkers.<sup>28,29</sup> They have, however, considered only the 1:1 association and the spread in their data - especially for the chromate system - is far too large to permit a discussion of the thermodynamics of the association process. It was hence considered to be of great interest to perform a more thorough investigation of these two systems in  $(\text{K},\text{Na})\text{NO}_3$  in order to obtain reliable data. Some emf titrations were performed with tungstate but because of irreproducible results this investigation was not continued.

Quasi lattice models<sup>30,31</sup> have often been applied to rationalize the thermodynamic properties of dilute melts. These models regard the melt as consisting of cationic and anionic interpenetrating sub-lattices with fixed coordination numbers of the ions. Complex formation is regarded as due to specific non-ionic interactions between central ion and ligand. Temperature independence of the specific interaction energy parameter has frequently been taken as a support for the model and it has been proven to hold in simple systems, especially in those with univalent monoatomic ions of about equal size. The model has - with ambiguous results - been applied to asymmetric systems with polyvalent polyatomic ions in alkali nitrate melts.<sup>21, 28, 29, 32</sup> One aim of this study has been to obtain precise information on the general applicability of the theory to such systems.

In general it is highly desirable to use various independent experimental methods in order that systematic misinterpretations may be revealed when

the composition and stability of complex ions are studied. In this study emf measurements of Ag(I) concentration cells and solubility measurements have been performed and in the case of the  $\text{Ag(I)}\text{-CrO}_4^{2-}$  system some spectrophotometric information has also been gained.<sup>III</sup> Thermodynamic parameters for the formation of  $\text{AgOx}^{(q-1)-}$  have been estimated from the temperature dependence of  $\Delta G^0$  for that process as measured by emf titrations. Direct determination of  $\Delta H_1^0$  by calorimetric measurements would of course have been preferable but no method of acceptable accuracy in melts at elevated temperatures is available at present.

From previous studies<sup>33</sup> it is known that solid solutions are often formed when solid salts are equilibrated with alkali nitrate melts. The ions of the solvent which are present in large concentrations have a tendency to replace ions in the solid phase. This phenomenon appears to be much more frequent in solubility studies of complex formation in ionic melts than in similar studies involving molecular solvents at ambient temperatures. As a consequence it has become necessary to measure the composition of the solids and to evaluate the activity - composition relations. The comparatively rapid equilibration between melt and solid solution makes such studies feasible.

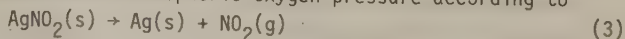
## EXPERIMENTAL SECTION

### General

Solubility and spectrophotometric measurements have been made at 280 °C - a reference temperature previously chosen at this laboratory. Emf measurements were performed at five temperatures between 250 and 350 °C as well, in order to examine the temperature dependence of the complexation. Table 1 surveys the oxoanions studied and the experimental methods used in each case.

The molybdate, chromate and iodate systems have been studied by solubility methods,<sup>34</sup> both with Ag(I) in excess over oxoanion in the melt and vice versa. Because of the low solubility of alkali phosphate in nitrate melts this system is studied only with Ag(I) in excess over orthophosphate.

As  $\text{AgNO}_2$  is decomposed under atmospheric oxygen pressure according to



no solubility study of this system could be performed.

Table 1. Oxoanions studied and the experimental methods used in each system.

| Oxoanion            | Experimental methods |            |                   |
|---------------------|----------------------|------------|-------------------|
|                     | Emf                  | Solubility | Spectrophotometry |
| $\text{NO}_2^-$     | X                    |            |                   |
| $\text{IO}_3^-$     | X                    | X          |                   |
| $\text{CrO}_4^{2-}$ | X                    | X          | X                 |
| $\text{MoO}_4^{2-}$ | X                    | X          |                   |
| $\text{PO}_4^{3-}$  | X                    | X          |                   |

Visible spectra of melts containing Ag(I) and chromate ions have been recorded. Only qualitative information could be obtained as the absorption appears near the UV-absorption edge of the nitrate solvent.<sup>III</sup>

The studied concentration ranges are limited by such factors as the solubility of the silver salts, activity factors deviating from unity, interfering reactions and methods of measurements.

### Chemicals

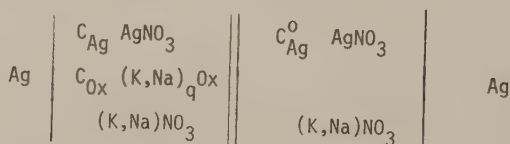
Commercially available p.a. grade nitrates and alkali metal oxoanion salts were <sup>used</sup> without further purification in all experimental work. Silver molybdate and silver phosphate were prepared by precipitation from aqueous solutions of silver nitrate and the appropriate sodium oxoanion salt. Silver chromate and iodate were commercial preparations from Merck and BDH Chemicals Ltd. The purity of the silver salts was checked by measuring their silver contents. All salts were easily dried at 120 °C except for  $\text{K}_3\text{PO}_4$ . Potassium phosphate was dried at successively higher temperatures (starting at 120 °C and ending at 500 °C) and then under vacuum at 200 °C.

The equimolar mixture of  $\text{KNO}_3$  and  $\text{NaNO}_3$  was prepared by grinding the pre-dried components together for several hours to a fine-grained powder, followed by further drying at 120 °C. Equimolar  $(\text{K,Na})_2\text{CrO}_4$  and  $(\text{K,Na})\text{IO}_3$  were prepared by a similar process. The 1:10 byweight mixture of  $\text{K}_3\text{PO}_4$

and  $(K,Na)NO_3$  used in the emf titrations was prepared by grinding the dried salts together. This mixture was dried repeatedly under vacuum prior to each titration.

### Emf measurements

The following cell was used in all systems



where  $C_{Ox}$  is the total concentration of oxoanion,  $Ox^{q-}$ . The measurements were performed in a solid aluminium block high-temperature thermostat. Details have been described elsewhere.<sup>20,35</sup> The test melt was kept in a large Pyrex glass vessel and agitated by a Pyrex glass stirrer. Reference half-cells were tubes of Pyrex glass, mounted with a ceramic plug,<sup>I</sup> supplied by Radiometer Copenhagen, dipping into the test melt. The furnace is equipped with stoppered observation tubes making visual observation of the systems possible. Additions of alkali oxoanion salts were made through a glass funnel which was temporarily immersed through the cover. The emfs were measured repeatedly by four different electrode combinations by an automatic datalogging unit.<sup>I</sup>

Equimolar mixtures of  $(K,Na)IO_3$  and  $(K,Na)_2CrO_4$  were added. Pure  $NaNO_2$  was used since  $KNO_2$  was difficult to handle in the anhydrous state. Molybdate was added as  $Na_2MoO_4$ . In both cases the K:Na ratio was at most shifted from 1:1 to 1:1.04 in the melt due to the addition of pure sodium salts which was considered to have negligible effect on the complex stabilities under study. Because of the low solubility of  $Ag_3PO_4$  only small amounts of phosphate could be added. In order to make accurate weighings of the additions a 1:10 mixture of  $K_3PO_4$  and  $(K,Na)NO_3$  was used.

## Solubility measurements

Equilibrations of the solubility systems were performed in Pyrex tubes thermostated in aluminium block furnaces. Motor-driven Pyrex stirrers were used for agitation. The furnace construction permits occasional visual observation of the systems. Equilibration times due to the formation of solid solutions were such that all systems had to be agitated for at least 48 h. After the stirring was stopped the solid phase settled rapidly and left a perfectly clear melt. Samples were withdrawn from the melt with pre-heated Pyrex pipettes, quenched and analysed in aqueous solution. Occasionally the samples were filtered by suction through a hot fine porosity glass filter tube immersed in the melt, but no effects on the measured solubilities could ever be observed.

The equilibrium composition of the solid phase was calculated from the difference between added and found amounts of various ions in the melt. This calculation gives meaningful results only when a sufficient amount of solid phase is used which is the reason for the relatively large quantities of silver oxoanion salts used. Solid phases of different compositions were investigated by X-ray powder diffraction at room temperature.

## Light absorption spectra

A Unicam SP 700 spectrophotometer was used. The optical cells were kept in an isolated aluminium block thermostat with an outer water-cooled jacket<sup>13</sup>. Spectra were recorded with 10 mm fused silica cells with pure  $(K,Na)NO_3$  melt as reference.

## SOLID PHASES AND SOLUBILITIES

When determining the stability of complex species by solubility methods it is evident that the composition of the solid has to be known exactly, and systems with varying composition of the solid have not often been studied.<sup>34</sup>

Recently a method of determining the activity of components in solid solutions which participate in heterogenous equilibria coupled to complex formation equilibria in the liquid phase has been outlined.<sup>10,33</sup> Since all salts  $Ag_qO_x$  studied dissolve the corresponding alkali salt from the

melt this method of determining activities has been used. Experiments with pure  $\text{KNO}_3$  and pure  $\text{NaNO}_3$  solvents have demonstrated that only solid solutions  $(\text{Ag},\text{Na})_q\text{O}_x$  are formed. The solid solutions are close to  $T_{\text{mix}}^{\text{ideal}}$ <sup>36</sup> for low mole fractions of  $\text{Na}_q\text{O}_x$ ,  $x_2$ , which means that the relation  $a_1 = x_1^q$ , where  $a_1$  and  $x_1$  are activity and mole fraction of  $\text{Ag}_q\text{O}_x$ , respectively, holds fairly well. This relation is deduced from a model that considers a cationic substitutional solution with the cations randomly mixed on fixed cation positions with negligible enthalpy of mixing. At larger  $x_2$  values positive deviations from ideality appear in all systems. In cases when phase transitions in the solid occur these deviations are rather abrupt.<sup>II,III</sup> Table 2 surveys the solid solutions studied.

For chromate and iodate phase transitions in the solid solutions have been detected. These are easily revealed if  $x_2$  is plotted against concentration of the oxoanion in the melt. In such a plot a large change in  $x_2$  in a narrow oxoanion concentration range is an indication of a phase transition (c.f. fig 1).

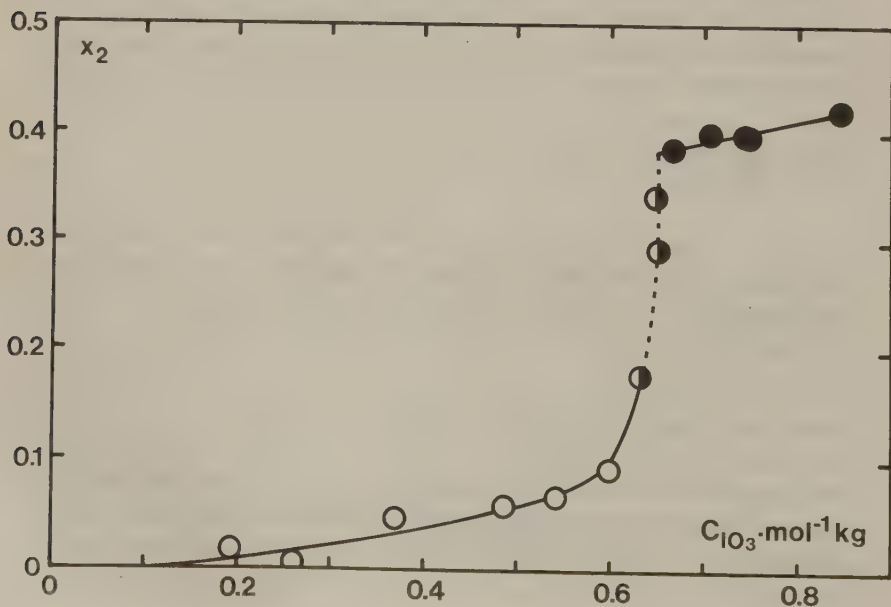


Fig. 1. Fraction of  $\text{NaIO}_3$ ,  $x_2$ , in the solid  $(\text{Ag},\text{Na})\text{IO}_3$  phase as a function of total concentration of  $\text{IO}_3^-$  in the melt.  $T = 553 \text{ K}$ .<sup>II</sup>

X-ray powder diffraction studies at room temperature have confirmed the formation of new phases referred to as "Na-rich phases" in Table 2. The Na-rich phases which occur after structural rearrangements could be properly indexed on the basis of an orthorhombic symmetry for  $(\text{Ag,Na})\text{IO}_3^{\text{II}}$  and a monoclinic symmetry for  $(\text{Ag,Na})_2\text{CrO}_4^{\text{III}}$ . In the  $(\text{Ag,Na})_2\text{CrO}_4$  system it is quite clear that at least one more phase transition must occur between  $x_2=0.9$  and  $x_2=1$ . A very rapid change in  $x_2$  appears in the phosphate system too but it can not be accurately traced to the point of complete transition due to the low solubility of alkali phosphate.<sup>V</sup>

Table 2. Survey of the solid solutions, solid phase transitions and maximum fraction of sodium salts studied at 553 K.

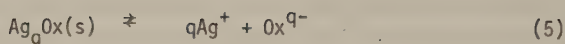
| Solid solution                 | Maximum $x_2$ studied | Lowest $x_2$ in Na-rich phase |
|--------------------------------|-----------------------|-------------------------------|
| $(\text{Ag,Na})\text{IO}_3$    | 0.42                  | $0.38 \pm 0.01$               |
| $(\text{Ag,Na})_2\text{CrO}_4$ | 0.88                  | $0.53 \pm 0.05$               |
| $(\text{Ag,Na})_2\text{MoO}_4$ | 0.60                  | -                             |
| $(\text{Ag,Na})_3\text{PO}_4$  | 0.16                  | $0.1 - 0.2$                   |

In the  $(\text{Ag,Na})_2\text{MoO}_4$  system a continuous range of solid solutions is formed.<sup>IV</sup> No phase transition can be detected either from thermodynamic or from X-ray measurements.  $\text{Ag}_2\text{MoO}_4$  and  $\text{Na}_2\text{MoO}_4$  have cubic structures and are isostructural.<sup>37,38</sup> X-ray powder diffraction on a sample with  $x_2=0.33$  gave an edge length of this material which is identical to the weighted average for the pure components. However, the solid solutions display positive deviations from ideality which are very well rationalized by the regular solution model.<sup>39</sup>  $\text{Ag}^+$  and  $\text{Na}^+$  can thus be regarded as randomly mixed on the cation positions with ideal entropy of mixing but a nonzero heat of mixing. The interaction parameter  $A$ , related to  $\Delta H_{\text{mix}}$  for



as  $A = \Delta H_{\text{mix}}(x_1 \cdot x_2)^{-1}$  (with  $x_1 + x_2 = 1$ ) is  $9.6 \pm 0.5 \text{ kJmol}^{-1}$  for the  $\text{Ag}^+ - \text{Na}^+$  mixing, which is the same value as has been found for the formation of  $(\text{Ag,Na})\text{Br}$  solid solutions.<sup>10</sup>

Solubility measurements give estimates of the equilibrium constants,  $K_s$ , of the simplified dissolution reaction



which are given in Table 3.

Table 3.  $K_S$  for silver oxoanion salts  $\text{Ag}_q\text{Ox}$  in molten equimolar  $(\text{K},\text{Na})\text{NO}_3$  at 553 K.

| Salt                             | $\text{AgIO}_3$               | $\text{Ag}_2\text{CrO}_4$     | $\text{Ag}_2\text{MoO}_4$     | $\text{Ag}_3\text{PO}_4$       |
|----------------------------------|-------------------------------|-------------------------------|-------------------------------|--------------------------------|
| $K_S/(\text{mol kg}^{-1})^{q+1}$ | $(1.0 \pm 0.1) \cdot 10^{-4}$ | $(6.4 \pm 0.5) \cdot 10^{-6}$ | $(2.3 \pm 0.1) \cdot 10^{-6}$ | $(6.9 \pm 2.1) \cdot 10^{-12}$ |

These values are, except for  $\text{Ag}_3\text{PO}_4$ , obtained from both ligand and central ion solubility studies, and in those cases, where the estimates from the two branches of the solubility curves differ, an average is given. The value for  $\text{Ag}_3\text{PO}_4$  has been obtained by a combination of solubility and emf data.<sup>V</sup> In a preliminary experiment, where complex formation and solid solution formation were not considered,  $K_S$  for  $\text{Ag}_2\text{WO}_4$  was estimated to  $1 \cdot 10^{-6} \text{ mol}^3 \text{kg}^{-3}$ .<sup>40</sup> The  $K_S$  values show the same trends as in aqueous solution but the solubilities are much lower in the melts, which indicates that the ions are more strongly solvated in aqueous solution than in the melts. For  $\text{Ag}_2\text{CrO}_4$  the solubility in equimolar  $(\text{K},\text{Na})\text{NO}_3$  has been determined previously by spectrophotometry<sup>41</sup> and emf titrations.<sup>42</sup> Lower values of  $K_S$  were obtained but the discrepancies are obviously due to the formation of solid solutions which has not been considered in those studies, e.g. refs. 41 and 42.

The solubility of the alkali oxoanion salts in silver(I) free melts has been measured. These values are given in Table 4 together with errors estimated from the spread of the analyses.

Table 4. Solubility,  $s$ , of  $(\text{K},\text{Na})_q\text{Ox}$  in the absence of  $\text{Ag}(\text{I})$  in equimolar  $(\text{K},\text{Na})\text{NO}_3$  at 553 K.

| $\text{Ox}^{q-}$       | $\text{IO}_3^-$ | $\text{CrO}_4^{2-}$ | $\text{MoO}_4^{2-}$ | $\text{PO}_4^{3-}$            |
|------------------------|-----------------|---------------------|---------------------|-------------------------------|
| $s/\text{mol kg}^{-1}$ | $\sim 1.3$      | $0.26 \pm 0.01$     | $0.17 \pm 0.01$     | $(2.3 \pm 0.2) \cdot 10^{-3}$ |

Except for  $\text{IO}_3^-$  these solubilities are lower than in aqueous solution. The larger solubility of these salts in aqueous solution is probably due both to protolysis and stronger ion solvation in water. There is a strong correlation between charge of the oxoanion and the solubility of the alkali salts in the nitrate melt.

#### COMPLEX SPECIES AT 553 K

Shorthand notations  $\text{Ag}^+$ ,  $\text{Ox}^{q-}$  and  $\text{Ag}_m\text{Ox}_n^{(m-nq)}$  are used for species in the melts which might have been better described as solvated with  $\text{K}^+$ ,  $\text{Na}^+$  or  $\text{NO}_3^-$ . No direct conclusions can be drawn about solvation from this kind of measurement, since the activity of the solvent cannot be varied independent of other activities. Since, however, the solvent activity can be regarded as effectively constant in these dilute systems, there is no need for any knowledge about the solvation. The stability constants are thus defined as

$$\beta_{mn} = \frac{[\text{Ag}_m\text{Ox}_n^{(m-nq)}]}{[\text{Ag}^+]^m [\text{Ox}^{q-}]^n} \quad (6)$$

Rather weak complexes are expected to be formed between  $\text{Ag}^+$  and the oxoanions. The  $\text{Ag(I)}$  complexes with the softer halide ions in molten  $(\text{K},\text{Na})\text{NO}_3$  are much more stable as can be seen from  $\beta_{11}$  for the formation of  $\text{AgX}$  at 553 K :  $270 \text{ mol}^{-1}\text{kg}$  for  $\text{X}=\text{Br}$ <sup>11</sup> and  $4200 \text{ mol}^{-1}\text{kg}$  for  $\text{X}=\text{I}$ <sup>12</sup>.

The relative distribution of  $\text{Ag(I)}$  on different species  $\text{AgOx}_n^{(nq-1)}$  at the limit  $C_{\text{Ag}} \gg 0$  is given in fig. 2. No drastic effects of ionic charge differences of the ligands can be seen, although the stability of the 1:1 complex increases slightly for increasing negative charge of the anion. The qualitative resemblance between the systems is striking, however.  $\text{AgOx}^{(q-1)-}$  contributes at most 20-40% of  $C_{\text{Ag}}$  while  $\text{Ag(Ox)}_2^{(2q-1)-}$  is formed only in minute amounts. The fraction of  $\text{Ag(NO}_2)_2^-$  at large  $[\text{NO}_2^-]$  is, however, somewhat larger and increases more rapidly with increasing ligand concentration than the others. Fig. 3 gives the relative distribution on different species  $\text{Ag}_m\text{Ox}^{(q-m)-}$  as a function of  $[\text{Ag}^+]$  at the limit  $C_{\text{Ox}} > 0$ . Here the studied concentration ranges reflect the solubilities of the silver salts. The iodate, chromate and molybdate systems are rather alike with the fraction of the first complex at a maximum and the second complex becoming equally important at the largest  $[\text{Ag}^+]$  studied. Larger stability is dis-

played by the phosphate system where the complexes appear at much lower  $\text{Ag(I)}$  concentrations.

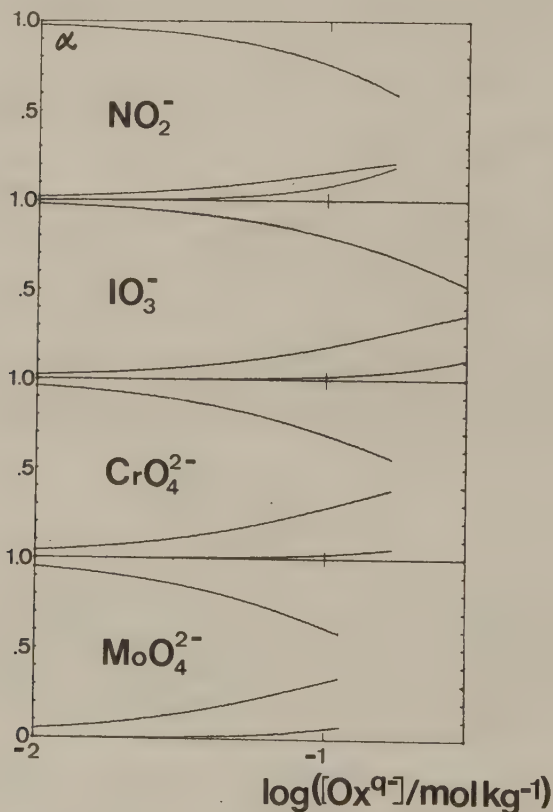


Fig. 2. Fraction of  $\text{Ag}^+$  in different complexes at the limit  $C_{\text{Ag}} \rightarrow 0$  at 553 K calculated from emf data of table 5. The curves represent from top to bottom in each diagram  $\text{Ag}^+$ ,  $\text{AgOx}^{(q-1)-}$ ,  $\text{Ag(Ox)}_2^{(2q-1)-}$  and are extended over the  $[\text{Ox}^{q-}]$  range experimentally covered.

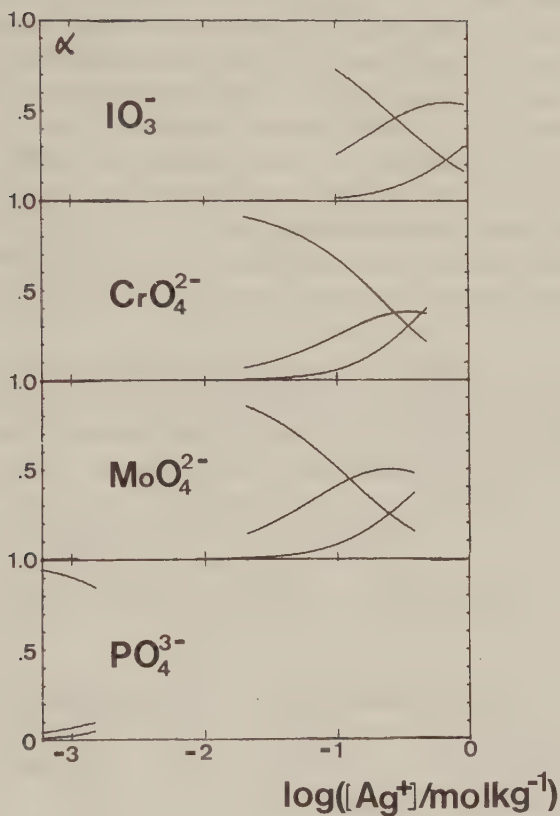


Fig. 3. Fraction of oxoanions in different complexes at the limit  $C_{Ox} \rightarrow 0$  at 553 K calculated from solubility and for phosphate from emf data of table 5. The curves represent in the left hand part of the figures from top to bottom  $Ox^{q-}$ ,  $AgOx^{(q-1)-}$  and  $Ag_2Ox^{(q-2)-}$  and are extended over the  $[Ag^+]$  range experimentally covered.

Solubility and emf measurements give the same over-all complexation pattern (table 5) although complexes  $\text{Ag}_2\text{Ox}^{(q-2)-}$  can be detected only by solubility measurements since they are formed only in melts with excess of  $\text{Ag(I)}$  over  $\text{Ox}^{q-}$ . One exception in this respect is the phosphate system where  $\text{Ag}_2\text{PO}_4^-$  is formed at rather low  $\text{Ag(I)}$  concentrations.<sup>V</sup> In aqueous solution  $\text{Ag(I)}$  complexes of both  $\text{NO}_2^-$ <sup>43</sup> and  $\text{IO}_3^-$ <sup>44</sup> have been detected. The same neutral and anionic complexes as in nitrate melts are found and even  $\text{Ag}_2\text{IO}_3^+$  has been reported.<sup>45</sup> Molybdate, chromate and phosphate are not easily studied in aqueous solutions due to low solubility of the silver salts, protonation and condensation reactions and no  $\text{Ag(I)}$  complexes have been characterized.

Table 5. Stability constants for  $\text{Ag(I)}$  oxoanion complexes in molten equimolar  $(\text{K,Na})\text{NO}_3$  at 553 K estimated with different experimental techniques. Unit of concentration is  $\text{mol kg}^{-1}$ . The limits of error define 95% confidence intervals.

| $\text{Ox}^{q-}$    | ref. | $\beta_{21}$               | $\beta_{11}$  | $\beta_{12}$  | method                                 |
|---------------------|------|----------------------------|---------------|---------------|----------------------------------------|
| $\text{NO}_2^-$     | I    | -                          | $2.1 \pm 0.3$ | $11 \pm 1$    | emf                                    |
| $\text{IO}_3^-$     | II   | -                          | $2.3 \pm 0.1$ | $2.4 \pm 0.7$ | emf                                    |
|                     |      | -                          | $2.1 \pm 0.7$ | $2.2 \pm 0.8$ | sol. $C_{\text{IO}_3} > C_{\text{Ag}}$ |
|                     |      | $2.1 \pm 1.0$              | $3.5 \pm 1.0$ | -             | sol. $C_{\text{Ag}} > C_{\text{IO}_3}$ |
| $\text{CrO}_4^{2-}$ | III  | -                          | $4.1 \pm 0.1$ | $3.6 \pm 1.1$ | emf                                    |
|                     |      | -                          | $4.2 \pm 2.6$ | $4 \pm 10$    | sol. $2C_{\text{Cr}} > C_{\text{Ag}}$  |
|                     |      | 8 t 3                      | $3.6 \pm 1.2$ | -             | sol. $C_{\text{Ag}} > 2C_{\text{Cr}}$  |
| $\text{MoO}_4^{2-}$ | IV   | -                          | $5.2 \pm 0.2$ | $10 \pm 3$    | emf                                    |
|                     |      | -                          | $3 \pm 3$     | $2 \pm 20$    | sol. $2C_{\text{Mo}} > C_{\text{Ag}}$  |
|                     |      | $16 \pm 6$                 | $8 \pm 3$     | -             | sol. $C_{\text{Ag}} > 2C_{\text{Mo}}$  |
| $\text{PO}_4^{3-}$  | V    | $(2.7 \pm 0.5) \cdot 10^4$ | $78 \pm 11$   | -             | emf                                    |

In table 5 all stability constants measured at 553 K are compared. Three different estimates of  $\beta_{11}$  for the iodate, chromate and molybdate systems are given. These values agree very well for all systems with the possible exception of the  $\beta_{11}$  value of the molybdate system which, however, is impaired

by wider limits of error. It is quite clear from the estimated errors that emf measurements give the most precise estimates of the stability constants and only constants obtained by this method have been used when the variation with temperature was studied. Larger errors are as a rule found for  $\beta_{12}$  and  $\beta_{21}$  because of the lower fractions of the 1:2 and 2:1 complexes in the composition range that could be covered by the experiments.

Spontaneous formation of  $\text{NO}_2^-$  in  $(\text{K},\text{Na})\text{NO}_3$  melts at elevated temperatures has been studied by Kust and Burke.<sup>23</sup> It is clear from the stability constants for  $\text{AgNO}_2$  and  $\text{Ag}(\text{NO}_2)_2^-$  that the low concentrations of  $\text{NO}_2^-$  from the thermal decomposition of  $\text{NO}_3^-$  in a normal atmosphere of laboratory air do not to any measurable extent affect the concentration of free silver ions below 623 K in  $(\text{Ag},\text{K},\text{Na})\text{NO}_3$  melts.<sup>I</sup> The  $\text{Ag}(\text{I})$  association with  $\text{NO}_2^-$  spontaneously formed can thus be considered as negligible when studying other systems in this solvent. It is interesting to note that the  $\text{AgIO}_3$  and  $\text{AgNO}_2$  complexes have about the same stability at 553 K but they owe their stability to different thermodynamic factors which will be discussed below.

The complexation of the chromate system is somewhat weaker than that of the molybdate system, which is in harmony with the higher solubility of  $\text{Ag}_2\text{CrO}_4$ . Sacchetto et al. have given  $\beta_{11}$  values for  $\text{AgCrO}_4^-$  and  $\text{AgMoO}_4^-$  in  $(\text{K},\text{Na})\text{NO}_3$  melts at different temperatures.<sup>28,29</sup> They have, however, not considered the formation of  $\text{AgOx}_2^{(2q-1)-}$  which has been proven to be necessary by the present study. Hence, no good estimates of  $\Delta H_1^0$  and  $\Delta S_1^0$  can be made from their set of  $\beta_{11}$  values which are not comparable to those of this study.

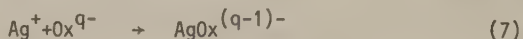
Visible spectra of chromate-containing melts with and without  $\text{Ag}(\text{I})$  show that the absorption peak of  $\text{CrO}_4^{2-}$  at 371 nm in pure  $(\text{K},\text{Na})\text{NO}_3$  is shifted towards lower energies when the melt contains  $\text{Ag}(\text{I})$  as well. This band is not changed when the charge density of the alkali ion in the  $\text{CrO}_4^{2-}$  surrounding is varied from  $\text{Li}^+$  to  $\text{Cs}^+$ <sup>46</sup> so the effect of rather low  $\text{Ag}^+$  concentrations is remarkable. The spectra furnish strong evidence for the existence of complexes with chemical interaction between  $\text{Ag}(\text{I})$  and  $\text{CrO}_4^{2-}$  which is fundamentally different from the alkali metal  $-\text{CrO}_4^{2-}$  interactions in nitrate melts.<sup>III</sup>

It was not possible to determine  $K_s$  for  $\text{Ag}_3\text{PO}_4$  separately from the solubility measurements, which is the reason why no stability constants from this kind of measurement are given in Table 5. When the stability constants from the potentiometric and solubility studies were combined a value of  $K_s$

could be estimated and a good agreement between the data from the two methods was achieved. The potentiometric study indicated that the complexes  $\text{AgPO}_4^{2-}$  and  $\text{Ag}_2\text{PO}_4^-$  were formed and that they are more stable than the corresponding complexes of the other oxoanions. The limited solubility of silver and alkali phosphate makes the concentration range available for these measurements narrow and the precision in  $\beta_{11}$  for  $\text{AgPO}_4^{2-}$  is lower than for the other 1:1 complexes in this study.<sup>V</sup>

## THERMODYNAMICS OF THE 1:1 COMPLEX FORMATION PROCESS

Due to the fact that  $\beta_{21}$  and  $\beta_{12}$  are as a rule impaired with wider limits of uncertainty than  $\beta_{11}$  the discussion is limited to  $\Delta H_1^0$  and  $\Delta S_1^0$  of the first complexation step, schematically written as



From a theoretical point of view process (7) is also the simplest possible reaction step, starting for all ligands with the same acceptor configuration.

Most studies of complex association in molten alkali nitrates have concerned halide complexes. Fig. 4 shows results from literature data on Ag(I) association with the halides. The standard states refer to unity ionic fractions. The figure has been constructed from primary data of refs. 21 and 47-52. As  $\Delta G_1^0$  is an apparently linear function of temperature  $\Delta H_1^0$  and  $\Delta S_1^0$  can be estimated from equ.(1). The thermodynamic pattern predicted from the classification in (a) - (b) terms in aqueous solution is found in nitrate melts too. AgF is the weakest complex and AgI and the pseudohalide complex AgCN are the strongest ones.  $\Delta H_1^0$  is  $\approx 0$  for  $\text{F}^-$  association with  $\text{Ag}^+$  to AgF and decreases monotonously through the halide series to  $-40 \text{ kJmol}^{-1}$  for  $\text{I}^-$ , whereas  $\Delta S_1^0$  exhibits very small variations ( $12-17 \text{ JK}^{-1}\text{mol}^{-1}$  for all halides).  $\text{CN}^-$  has been included here as the only monovalent polyatomic ligand studied prior to this work. For the formation of AgCN the following estimates can be made by use of the data from ref. 21:  $\Delta H_1^0 \approx -6 \text{ kJmol}^{-1}$  and  $\Delta S_1^0 \approx 90 \text{ Jmol}^{-1}\text{K}^{-1}$ . This is in contrast to the normal (b)-(b) pattern in aqueous solution. No obvious explanation for this behaviour in ionic melts can be given at present, but it should be noted that entropy contributions due to changes in internal degrees of freedom alone can certainly not explain the large  $\Delta S_1^0$  for the complexation process.

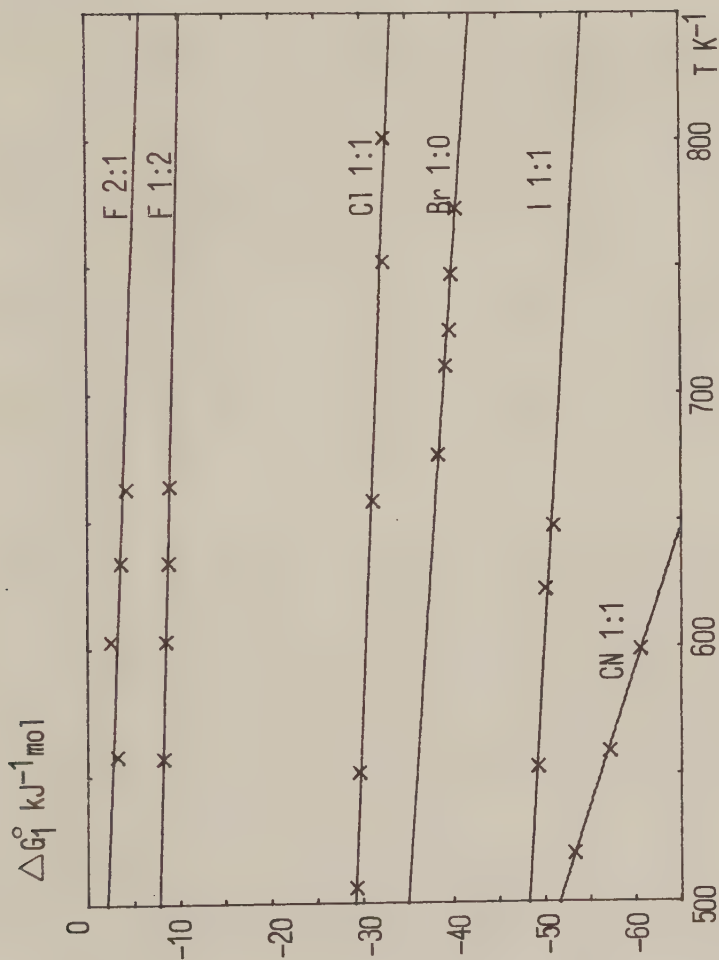


Fig. 4.  $\Delta G_f^0$  versus  $T$  for  $\text{Ag}^+ + \text{X}^- \rightarrow \text{AgX}$  in alkali nitrate melts. The K:Na ratio and X are indicated on the lines. Primary data from refs. 21 and 47-52. The standard state refers to unity ionic fractions.

Table 6 gives estimates from this study of the thermodynamic parameters for the formation of 1:1 complexes with oxoanions. These parameters are calculated by linear regression according to eqn.(1). The graphs of  $\Delta G_1^0$  as a function of temperature are given in fig. 5 together with the experimental points.

Table 6. Enthalpy, entropy and free energy changes for the reaction  $\text{Ag}^+ + \text{Ox}^{q-} \rightarrow \text{AgOx}^{(q-1)-}$  in molten equimolar  $(\text{K}, \text{Na})\text{NO}_3$ . Stated errors are one estimated standard deviation.

| $\text{Ox}^{q-}$    | $\Delta H_1^0 / \text{kJ} \cdot \text{mol}^{-1}$ | $\Delta S_1^0 / \text{J} \cdot \text{mol}^{-1} \text{K}^{-1}$ | $\Delta G_1^0 / \text{kJ} \cdot \text{mol}^{-1}$ at 553 K |                              |
|---------------------|--------------------------------------------------|---------------------------------------------------------------|-----------------------------------------------------------|------------------------------|
|                     |                                                  |                                                               | calculated<br>( $\Delta H_1^0 - 553 \Delta S_1^0$ )       | experimental<br>(papers I-V) |
| $\text{NO}_2^-$     | $-23 \pm 1$                                      | $-15 \pm 2$                                                   | -14.7                                                     | $-14.3 \pm 0.4$              |
| $\text{IO}_3^-$     | $2.3 \pm 1.6$                                    | $31 \pm 3$                                                    | -14.8                                                     | $-14.7 \pm 0.3$              |
| $\text{CrO}_4^{2-}$ | $-6.0 \pm 1.5$                                   | $20 \pm 3$                                                    | -17.1                                                     | $-17.4 \pm 0.1$              |
| $\text{MoO}_4^{2-}$ | $-7.5 \pm 1.6$                                   | $20 \pm 3$                                                    | -18.6                                                     | $-18.5 \pm 0.2$              |
| $\text{PO}_4^{3-}$  | $-12.4 \pm 6.7$                                  | $33 \pm 12$                                                   | -30.6                                                     | $-30.9 \pm 0.7$              |

The thermodynamic parameters of Table 6 show that an analysis in terms of  $\Delta H_1^0$  and  $\Delta S_1^0$  reveals differences, which can not be detected from the  $\Delta G_1^0$  values alone. By comparison with complexes of the softer halides it is found that the entropy change upon complexation with oxoanions is of greater relative importance for the stability of the complexes, mainly because of the smaller  $-\Delta H_1^0$  values for the oxoanion associations. The  $\text{Ag(I)}-\text{NO}_2^-$  system makes a remarkable exception from this general trend. The ambidentate character of  $\text{NO}_2^-$  makes nitrogen coordination possible, and the relatively large value of  $-\Delta H_1^0$  suggests Ag-N bond formation.<sup>I</sup>

The thermodynamic patterns of the  $\text{AgIO}_3$  and  $\text{AgNO}_2$  complexations show - together with the previously discussed thermodynamics of  $\text{AgCN}$  formation - that the "classical" model of complex formation in dilute ternary ionic systems is not universally applicable. The generally accepted view is that a specific non-ionic interaction between ligand and central ion leads to a negative value of  $\Delta H_1^0$  and a comparably small  $\Delta S_1^0$ , mainly determined by configurational contributions from ionic interchanges in a fixed lattice-

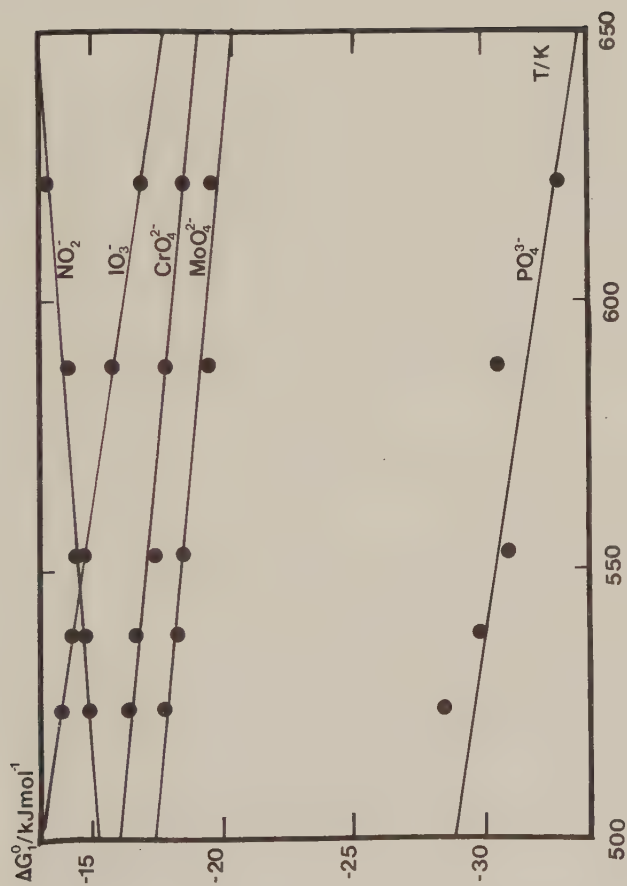
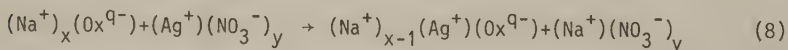


Fig. 5.  $\Delta G_f^0$  versus  $T$  for  $\text{Ag}^+ + \text{O}_x\text{O}^{q-} \rightarrow \text{AgO}_x(\text{q}-1)^-$  in equimolar  $(\text{K}, \text{Na})\text{NO}_3$ . The appropriate oxoanions are indicated on the lines. The standard state refers to unity ionic fractions.

like environment of the central ion. In the case of  $\Delta H_1^0$  for  $\text{AgNO}_2$  formation this prediction is not contradicted but the negative  $\Delta S_1^0$  is inconsistent with the model. For the formation of the  $\text{AgIO}_3$  complex  $\Delta H_1^0 \approx 0$  and it is the gain in entropy alone that stabilizes the complex. The complexation processes are probably essentially different on a molecular level and can in neither case be properly described by simple lattice exchange arguments.

The  $\text{CrO}_4^{2-}$  and  $\text{MoO}_4^{2-}$  complexation are very similar although a somewhat higher stability of  $\text{AgMoO}_4^-$  is found<sup>IV</sup>.

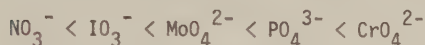
The influence of the charge of the oxoanion on the stability of the  $\text{AgOx}^{(q-1)-}$  complexes is low even if there is a slight trend that the stability increases for increasing negative charge of the anion. The influence of the charge on  $\Delta H_1^0$  seems to be more clear-cut. In these considerations the  $\text{NO}_2^-$  complex is not included due to the different coordination mode suggested for that complex. It is not clear which of the solvent cations in the coordination shell of the oxoanion that is exchanged for  $\text{Ag}^+$  during the formation of the complexes but since the  $\text{Na}^+$  ion is smaller than  $\text{K}^+$  the oxoanions of larger charge density should be predominantly solvated by  $\text{Na}^+$ . An exchange of  $\text{Na}^+$  for the larger  $\text{Ag}^+$  in the coordination sphere of  $\text{Ox}^{q-}$  according to



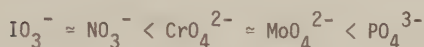
is, however, energetically unfavourable for oxoanions having  $q > 1$ , if ionic hard sphere interactions alone were operative. The energy required for such a process would increase with increasing negative charge density of  $\text{Ox}^{q-}$ . Since, however, the opposite trend is actually found, i.e.  $-\Delta H_1^0$  increases with increasing oxoanion charge, it is concluded that the interaction between  $\text{Ag(I)}$  and the oxoligands is of a considerable covalent character, increasing in strength with increasing ionic charge of the oxoligands. The spectral investigation of melts containing  $\text{AgCrO}_4^-$  and  $\text{Ag}_2\text{CrO}_4$  complexes<sup>III</sup> also shows that  $\text{Ag-O}$  bonds of appreciable covalent character are formed with this kind of oxoanion. These conclusions about the different type of bonding to oxoanions of  $\text{Ag(I)}$  and the alkali ions is in agreement with previous findings of Baran and coworkers<sup>53</sup> based on vibrational spectra of solid oxoanion salts of various metal ions.

Optical basicities, which Duffy<sup>54,55</sup> has shown to correlate well with such different parameters as glass properties and Hammett acidities, are expected to reflect the electron donating power via oxygen in the oxoanions. These

basicities do not show a straightforward correlation to  $\Delta H_1^0$  for Ag(I) complexation with  $\text{IO}_3^-$ ,  $\text{CrO}_4^{2-}$ ,  $\text{MoO}_4^{2-}$  and  $\text{PO}_4^{3-}$ , however. The optical basicities predict the bond strength order of the  $\text{AgOx}^{(q-1)-}$  complexes as,



whereas  $-\Delta H_1^0$  increases in the order,



Better correlation might be found if some solvent cation is included into the chemical unit for which the basicity is calculated, since cationic solvation effects seem to be important for the polyatomic oxoanions. Such calculations would require knowledge of the cationic structure around the oxo-ligands which is not available at present.

This study has shown - mainly by the  $\Delta S_1^0$  values - that the quasi-lattice model is not applicable to systems of this type. From a theoretical point of view there are two fundamental reasons for the inapplicability. First the ionic charge asymmetry between solvent and solute ions, and secondly changes in internal degrees of freedom of the polyatomic oxoanions, that make the entropy change deviate from the ideal configurational one. In spite of these facts efforts have been made to apply the model to such systems.<sup>21,28,29,32</sup> Divergences have been explained as changes in internal degrees of freedom<sup>21,32</sup> or mixed solvent effects.<sup>28,29</sup> For the monovalent ions  $\text{NO}_2^-$  and  $\text{IO}_3^-$  there are no charge asymmetry effects, but  $\Delta S_1^0$  is still in conflict with any reasonable quasi-lattice model prediction. The magnitude of  $\Delta S_1^0$  can not be explained by "internal entropy" or "mixed solvent" effects, and it is suggested that a large part of the entropy change is due to configurational contributions in excess of those predicted by the model. Better precision in the measurements on the  $\text{AgCrO}_4^-$  and  $\text{AgMoO}_4^-$  complexes in this study than those previously reported indicates marked deviations from the model and the deviations expected for the  $\text{Ag}^+ - \text{PO}_4^{3-}$  system have also been found.

Two possible ways of providing more information on  $\text{Ag}^+ - \text{Ox}^{q-}$  complexation in nitrate melts can be outlined here. The need for independent structural information in order to make a detailed description of the complex formation processes on a molecular level is obvious. The cation solvation of the oxoligand should be studied, and both the number and type of alkali

ions in the coordination shell should be known in mixed cation systems. Our knowledge could also be broadened by a study of some more oxoanion ligands by the methods described here. Some suitable candidates are the tetrahedral ions  $\text{ReO}_4^-$ ,  $\text{SO}_4^{2-}$  and  $\text{AsO}_4^{3-}$ .

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## Nitrite Complexes of Silver(I) in Molten Alkali Nitrates

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Potentiometric measurements with silver(I) concentration cells in melts of 1:1 (K, Na)NO<sub>3</sub> containing AgNO<sub>3</sub> and NaNO<sub>2</sub> have been performed in the temperature range 523K-623K. It is demonstrated that NO<sub>2</sub><sup>-</sup> acts as a fairly weak ligand for Ag(I). Complexes with the formal compositions AgNO<sub>2</sub> and Ag(NO<sub>2</sub>)<sub>2</sub><sup>-</sup> are detected and their stability constants are determined. The disproportionation reaction  $2 \text{AgNO}_2 \rightarrow \text{Ag}^+ + \text{Ag}(\text{NO}_2)_2^-$  is favoured by increased temperature. From estimated standard enthalpy and entropy changes it is suggested that the addition of a second NO<sub>2</sub><sup>-</sup> to Ag(I) according to  $\text{AgNO}_2 + \text{NO}_2^- \rightarrow \text{Ag}(\text{NO}_2)_2^-$  occurs with a considerable structural rearrangement of solvent NO<sub>3</sub><sup>-</sup> ions adjacent to silver. Application of the quasi-lattice formalism to the data gives temperature dependent specific interaction parameters  $\Delta\bar{A}_1$  and  $\Delta\bar{A}_2$ .  $(\partial(-\Delta\bar{A}_1)/\partial T)_{\underline{z}=5}$  can possibly be looked upon as a change in internal entropy, whereas it is highly doubtful if the basic assumptions of the theory hold for the second step.

## Introduction

From aqueous and solid state chemistry the nitrite ion is known to act as an ambidentate ligand, being capable of coordinating both via oxygens to give nitrito complexes and via the nitrogen lone pair, giving nitro complexes. Although hard or soft character of the metal atom would to some extent enhance the tendency to O- or N-coordination respectively, it seems that steric factors are most important in determining the coordination mode, at least in the solid state.<sup>1</sup>

The important role of nitrite ion in the fundamental chemistry of molten alkali metal nitrates has been elucidated in a number of studies on oxygen ion equilibria. This field of chemistry has been surveyed in a recent review by Kerridge.<sup>2</sup> So far, however, the ability of  $\text{NO}_2^-$  to complex metal ions in molten salts has received little attention.<sup>3</sup>

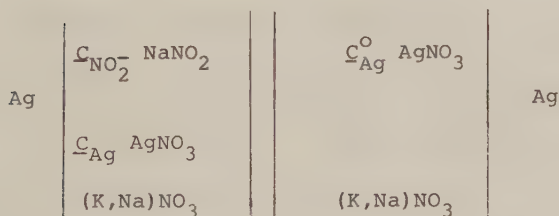
Boxall and Johnson<sup>4</sup> observed considerable shifts in the emf of silver(I) concentration cells as the solvent, molten  $\text{NaNO}_3$ , in one half-cell was gradually replaced by  $\text{NaNO}_2$  at  $309^\circ\text{C}$ . These shifts can be taken as an indication of a tendency of  $\text{Ag(I)}$  to complex with  $\text{NO}_2^-$  in the molten nitrate medium. We report results from a potentiometric study of the  $\text{Ag}^+ - \text{NO}_2^-$  association in dilute solutions in the "standard" solvent melt  $1:1(\text{K}, \text{Na})\text{NO}_3$ . The temperature and composition range accessible is limited by a number of potentially interfering reactions, such as the thermal

decomposition of solvent  $\text{NO}_3^-$  to  $\text{NO}_2^-$ , the thermal decomposition of  $\text{AgNO}_2$  and the oxidation of  $\text{NO}_2^-$  to  $\text{NO}_3^-$  by air oxygen. These interferences will be discussed in a later section, but it should be noted here that the thermal decomposition of  $\text{AgNO}_2$  makes the solubility technique, which has been successfully used in aqueous solutions,<sup>5-7</sup> inapplicable as a complement to the potentiometric measurements.

### Experimental

P.a. grade chemicals from Merck A.G. were used without further purifications. The  $(\text{K}, \text{Na})\text{NO}_3$  solvent was prepared and dried as described previously.<sup>8</sup> Nitrite was added as  $\text{NaNO}_2$  only, since  $\text{KNO}_2$  appeared to be difficult to handle in the anhydrous state. In this way the  $\text{K}:\text{Na}$  balance was at most shifted from 1:1 to 1:1.04 in the melt, which was considered to have a negligible influence on the complex stabilities under study.  $\text{NaNO}_2$  was dried at  $120^\circ\text{C}$  for at least 24 h and stored over  $\text{P}_2\text{O}_5$  prior to use.

The emf was measured for concentration cells



Here  $\underline{C}_{\text{NO}_2^-}$  and  $\underline{C}_{\text{Ag}}$  are total concentrations of nitrite and  $\text{Ag}(\text{I})$  respectively in the test melt, and  $\underline{C}_{\text{Ag}}^{\text{O}}$  correspondingly defines the total  $\text{Ag}(\text{I})$  concentration in the reference half-cell.

The melts were kept in Pyrex glass vessels in an aluminium block precision thermostat, fitted with a proportional temperature regulator, type CR/DHS/PID/SCR from Eurotherm, Worthing, England. Details of the furnace equipment, cell construction and electrodes can be found in previous papers.<sup>8,9</sup> In this work, however, the asbestos fibre junction between the half-cells was replaced by a ceramic plug (5 mm x 1 mm diam), supplied by Radiometer, Copenhagen. The long-time performance of the reference half cells was considerably improved by this replacement.

The cell was usually set up with  $\underline{C}_{\text{Ag}} = 1 \times 10^{-3} \text{ mol kg}^{-1}$  and  $\underline{C}_{\text{Ag}}^{\text{O}} = 3 \times 10^{-3} \text{ mol kg}^{-1}$ . The test melt was left with vigorous stirring for about 18 h. before any addition of nitrite was made. In this way an equilibrium concentration of  $\text{NO}_2^-$ , corresponding to the local partial pressure of oxygen in the laboratory air, was built up by thermal decomposition of  $\text{NO}_3^-$ .<sup>10</sup>

Successive additions of  $\text{NaNO}_2$  to the test melt were then made and the emf was measured repeatedly at constant temperature over four different electrode combinations after each addition by means of a Digiscan 10 PRC data logging unit from Mess+System Technik, München. The  $E$ -values were measured to  $\pm 0.05 \text{ mV}$ . Stable readings were as a rule obtained within 10 min after each addition of  $\text{NaNO}_2$ .

All series of measurements were duplicated at least once. Data were recorded at five different temperatures in the range

250°C-350°C. Maximum concentrations of nitrite at each temperature are given in Table I.

## Results and Discussion

Some General Considerations. The thermal decomposition of the nitrate melt according to

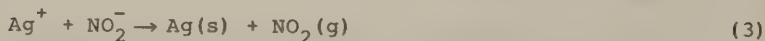


produces an equilibrium "background" concentration,  $\underline{C}_0$ , of  $\text{NO}_2^-$  at each temperature. From the data of Kust and Burke,<sup>10</sup> obtained in the range 568K-613K, we have estimated  $\underline{C}_0$  after correction to our laboratory air pressure of  $\text{O}_2$ , 0.2 atm, assuming constant  $\Delta H^\circ$  and  $\Delta S^\circ$  for process (1) in the range 523K-623K. The total concentration of nitrite,  $\underline{C}_{\text{NO}_2^-}$ , is then calculated as  $\underline{C}_{\text{NO}_2^-} = \underline{C}_0 + \underline{C}'$  in every melt under study. Here  $\underline{C}'$  is a nominal quantity, computed from the added amount of  $\text{NaNO}_2$ . The estimated  $\underline{C}_0$  values are actually negligible (Table I) and they may be impaired by substantial errors without violating our determination of the compositions and stabilities of the Ag(I) complexes.

In melts having a high concentration of  $\text{NO}_2^-$   $\underline{C}_{\text{NO}_2^-}$  can decrease with time due to two different processes. Firstly, the reversal of (1) occurs:



Secondly, in the absence of solid  $\text{AgNO}_2$  a reaction which can be described conveniently as<sup>11</sup>



may take place.

The kinetics of reaction (2) in 1:1 (K, Na) $\text{NO}_3$  has been thoroughly studied by Paniccia and Zambonin.<sup>12</sup> It may be inferred from their rate constants that the maximum average oxidation rate amounts to about  $1 \times 10^{-5} \text{ mol kg}^{-1} \text{ h}^{-1}$  in the most  $\text{NO}_2^-$  rich melts ( $C_{\text{NO}_2^-} = 0.1 \text{ mol kg}^{-1}$ ) at 623 K, so this process has no practical influence on the potentiometric measurements. Hence, the upper practical concentration limit for  $\text{NO}_2^-$  (and  $\text{Ag}^+$ ) is set by reaction (3). This process could be followed experimentally as a drift in the emf when the product  $[\text{Ag}^+][\text{NO}_2^-]$  becomes large. Consequently the maximum  $\text{NO}_2^-$  concentration that was used in the computations of stability constants,  $(C_{\text{NO}_2^-})_{\text{max}}$  in Table I, was determined by the requirement that stable emf readings should be recorded for at least 30 min.

Table I reviews the experimental material.

Treatment of Experimental Data. Liquid junction potentials are negligible within the range of  $\text{NO}_2^-$  concentrations used in this study.<sup>4</sup> The quantity  $C_{\text{Ag}}/[\text{Ag}^+]$  can thus be calculated from the emf of the cell as

$$\left( \frac{C_{\text{Ag}}}{[\text{Ag}^+]} \right)_{\underline{c}} = \exp \left[ \frac{F}{RT} (\underline{E}_0 - \underline{E}_{\underline{c}}) \right] \quad (4)$$

Here the index  $\underline{c}$  denotes quantities pertaining to systems with  $C_{\text{NO}_2^-} = \underline{c}$ , and  $\underline{E}_0$  refers to  $C_{\text{NO}_2^-} = 0$ . Experimental values of  $\underline{E}_0$  are, however, not strictly available due to the thermal decomposition of  $\text{NO}_3^-$ . The values used in the calculations are actually measured for  $C_{\text{NO}_2^-} = \underline{C}_0$ . By use of the stability constants, determined with these approximate  $\underline{E}_0$ , and eqn (5) (below) the errors introduced in  $(\underline{E}_0 - \underline{E}_{\underline{c}})$  with this approximation can be estimated to  $\leq 0.02$  mV, which is less than the accuracy in the measured emf. Therefore, no correction of  $\underline{E}_0$  to adjust for process (1) has to be made.

In a set of preliminary experiments at  $280^\circ\text{C}$  it was ascertained that  $C_{\text{Ag}}/[\text{Ag}^+]$  was independent of  $C_{\text{Ag}}$  within the concentration range accessible. All data were hence treated according to eqn (5) assuming mononuclear species only:

$$C_{\text{Ag}}/[\text{Ag}^+] = \sum_{\underline{i}=0}^N \beta_{\underline{i}} [\text{NO}_2^-]^{\underline{i}} \quad ; \quad \beta_0 = 1 \quad (5)$$

Here

$$\beta_{\frac{1}{2}} = [\text{Ag}(\text{NO}_2)_{\frac{1}{2}}]^{(1-\frac{1}{2})} [\text{Ag}^+]^{-1} [\text{NO}_2^-]^{-\frac{1}{2}} \quad (6)$$

is the over-all stability constant for  $\text{Ag}(\text{NO}_2)_{\frac{1}{2}}^{(1-\frac{1}{2})}$  according to the simplified equilibrium model



Figure 1 displays experimental results from two duplicate series of measurements at 280°C as an example of the spacing of data. The  $C_{\text{Ag}}/[\text{Ag}^+]$  data at 280°C and all other temperatures are well described by second degree polynomials in  $[\text{NO}_2^-]$ , i.e. by complexes with the formal compositions  $\text{AgNO}_2$  and  $\text{Ag}(\text{NO}_2)_2^-$ . Preliminary sets of  $\beta_{\frac{1}{2}}$  were obtained from regression analyses with the approximation  $[\text{NO}_2^-] = C_{\text{NO}_2}$ . Better values of  $[\text{NO}_2^-]$  to be used in an interactive process were obtained from

$$[\text{NO}_2^-] = C_{\text{NO}_2} - \bar{n} C_{\text{Ag}}, \quad (8)$$

where the average ligand number  $\bar{n}$  is calculated from the provisional constants. Only one cycle was necessary to obtain sufficient convergence in the parameter values. The results are given in Table II.

The data of Table II reveal that the general pattern from aqueous solution chemistry<sup>7</sup> - rather weak complexation

stopping with  $\text{Ag}(\text{NO}_2)_2^-$  - is followed in nitrate melts as well. It is noteworthy, however, that  $\text{Ag}(\text{NO}_2)_2^-$  becomes more important as the temperature is increased, indicating an entropy favoured second complexation step in nitrate melts. This can also be looked upon as a favourable disproportionation of the 1:1 species,



due to an entropy gain. The over-all complexation of silver is, however, fairly constant as the temperature is changed. This is clear from Figure 2 showing the fraction  $\alpha$  of silver present as  $\text{Ag}^+$ ,  $\text{AgNO}_2$  and  $\text{Ag}(\text{NO}_2)_2^-$  as a function of  $[\text{NO}_2^-]$  at 523 K and 623 K. At  $[\text{NO}_2^-] = 0.1 \text{ mol kg}^{-1}$  about 30% of  $\text{Ag}(\text{I})$  is complexed by  $\text{NO}_2^-$  irrespective of the temperature, whereas  $\text{AgNO}_2$  is the predominating complex at 523 K and  $\text{Ag}(\text{NO}_2)_2^-$  dominates at 623 K.

Estimates of Thermodynamic Parameters.  $\Delta H_i^0$  and  $\Delta S_i^0$  ( $i=1$  and 2) for the two successive steps of complexation, schematically written as



and



have been estimated from a study of  $\Delta G_{\pm}^{\circ} = -RT \ln K_{\pm}$  as a function of  $T$ ,  $K_{\pm}$  being the stepwise equilibrium constants for (10) and (11). The standard state chosen relates to unity ion fractions.

From Figure 3 it is seen that both  $\Delta G_1^{\circ}$  and  $\Delta G_2^{\circ}$  are good linear functions of  $T$ , so  $\Delta H_{\pm}^{\circ}$  and  $\Delta S_{\pm}^{\circ}$  have been estimated as constants by linear regression analysis. In doing so we have given every data point an individual weight proportional to  $(\sigma_{\pm}(T))^{-2}$ , where  $\sigma_{\pm}(T)$  is given by eqns (12) and (13) below.

$$\sigma_1(T) = RT \frac{\sigma(\beta_1)}{\beta_1} \quad (12)$$

$$\sigma_2(T) = RT \left\{ \left[ \frac{\sigma(\beta_1)}{\beta_1} \right]^2 + \left[ \frac{\sigma(\beta_2)}{\beta_2} \right]^2 \right\}^{\frac{1}{2}} \quad (13)$$

Here  $\sigma(\beta_{\pm})$  is the estimated standard deviation in  $\beta_{\pm}$  at the temperature in question. Intervals corresponding to  $2\sigma_{\pm}$  are marked around every point in Figure 3. The resulting parameters are given in Table III.

The first step of complexation is markedly exothermic, but the association is also disfavoured by a considerable loss in entropy. This thermodynamic pattern is analogous to what has been found for aqueous solutions.<sup>7</sup> For the second step, however, no such similarity is found. The process is highly endothermic and is energetically favoured by a remarkably large gain in entropy in the molten nitrate medium. No definite

explanation of this remarkable behaviour can of course be given here, but a qualitative interpretation will be suggested.

The first step (10) could be looked upon simply as a 1:1 exchange of  $\text{NO}_3^-$  for  $\text{NO}_2^-$  on an anionic quasi-lattice or alternatively an associative process involving a change in the Ag-nitrate interaction mode from bidentate to monodentate. The negative  $\Delta S_1^0$  may - at least in part - be due to a change in internal degrees of freedom for the  $\text{NO}_2^-$  and  $\text{NO}_3^-$  involved, and the large exothermic  $\Delta H_1^0$  may originate from a creation of a comparably strong Ag-N bond to  $\text{NO}_2^-$ . When the second ligand is to be added, structural demands of  $\text{Ag}(\text{NO}_2)_2^-$ , imposed by say a linear N-Ag-N geometry, would require a much larger number of Ag-nitrate oxygen bonds to be broken in step (11) (as compared to (10)), resulting in a positive  $\Delta H_2^0$ . Such a release of nitrate ions should also be associated with a predominantly configurational entropy gain.

A mechanistic description along these lines can qualitatively explain the thermodynamic difference between the two successive steps in melts as well as the contrast between the thermodynamics of the second step in water solution and nitrate melt. It should be remembered, however, that no clear-cut supporting structural evidence for preferential nitrogen coordination to Ag in solid compounds can be found. There are both O and N contacts with Ag in solid  $\text{AgNO}_2$ <sup>13</sup> as well as in the ferroelectric and paraelectric modifications of  $\text{AgNa}(\text{NO}_2)_2$ <sup>14</sup> and  $\text{Ag}(\text{NH}_3)_2\text{Ag}(\text{NO}_2)_2$ <sup>15</sup> - the two later compounds with orientational  $\text{NO}_2^-$  disorder.

Application of Quasi-Lattice Formalism. The quasi-lattice theory for pair association in reciprocal ionic melts<sup>16</sup> has previously been applied to 1:1 complexation reactions between silver(I) and a number of divalent oxoanions in alkali nitrate melts by Sacchetto and coworkers.<sup>17,18</sup> They found a reasonably good agreement between model and experimental results in one-component solvents as well as mixed cation solvents after modification of the model to account for temperature variations in the quasi-lattice association energy parameter  $\Delta A_1$  due to the presence of two different solvent cations.<sup>19</sup> Apparently, the anion charge inequality had no effect on the applicability of the model though structural rearrangements violating the basic assumptions of the theory are likely to occur when divalent ligand anions are mixed with  $\text{NO}_3^-$  ions.

In view of this our results clearly offer a good opportunity to test the applicability of the quasi-lattice model on association with a polyatomic ligand in a system of equally charged constituent ions. We calculated  $\Delta A_1$  and  $\Delta A_2$  for processes (10) and (11) using the straight-forward formalism of the generalized theory given by Blander.<sup>20</sup> The quasi-lattice coordination number  $\underline{z}$  was set equal to 5 in order to conform to the previous calculations by Sacchetto and coworkers.<sup>17,18</sup>

As might be expected from the magnitudes of  $\Delta S_1^0$  and  $\Delta S_2^0$  there is a considerable variation in  $\Delta A_1$  and  $\Delta A_2$  with temperature. The temperature dependence can be effectively

rationalized as

$$\Delta \underline{A}_i = \underline{a}_i + \underline{b}_i \cdot T \quad (14)$$

with constant values of  $\underline{a}_i$  and  $\underline{b}_i$  for  $i=1$  and 2. These parameters were estimated by linear regression analysis using the same weighing scheme as described for the study of  $\Delta \underline{G}_i^{\circ}$  vs.  $T$ . For  $\underline{a}_i$  the following values are found:  $\underline{a}_1 = (-19 \pm 2)$  kJ mol<sup>-1</sup> and  $\underline{a}_2 = (59 \pm 6)$  kJ mol<sup>-1</sup>. For  $\underline{b}_i$  we have  $\underline{b}_1 = (20 \pm 3)$  J K<sup>-1</sup> mol<sup>-1</sup> and  $\underline{b}_2 = (-133 \pm 12)$  J K<sup>-1</sup> mol<sup>-1</sup>. The parameters, referring to the same standard state as  $\Delta \underline{H}_i^{\circ}$  and  $\Delta \underline{S}_i^{\circ}$ , are given within 95% confidence limits.

Obviously, the positive value of  $\underline{b}_1$  cannot be explained by the presence of two different solvent cations, since the modified theory by Bombi and Sacchetto<sup>19</sup> predicts  $(\partial(\Delta \underline{A}_1)/\partial T)_{\underline{z}} \leq 0$ . In the present case it seems more reasonable to adopt the view that  $-\underline{b}_1 = (\partial(-\Delta \underline{A}_1)/\partial T)_{\underline{z}=5}$  largely expresses a change in internal entropy,  $\Delta \underline{S}_{int}$ , of the polyatomic ions exchanging on the anion sublattice of the melt. Actually  $\Delta \underline{S}_{int} = -20$  J K<sup>-1</sup> mol<sup>-1</sup> appears to be of a more reasonable order of magnitude than  $\Delta \underline{S}_{int} = 80$  J K<sup>-1</sup> mol<sup>-1</sup> which can be calculated (with  $\underline{z}=5$ ) for Ag<sup>+</sup> - CN<sup>-</sup> association in 1:1 (K,Na)NO<sub>3</sub> melts by use of data given by Manning and Blander.<sup>21</sup> This comparison is made here, since the study of Manning and Blander constituted the only source of information on univalent polyatomic ligand behaviour in nitrate melts prior to the present work.

As for the second step of association (11) the large negative value of  $b_2$  seems to be inconsistent with both "mixed solvent" and "internal entropy" explanations. For reasons already mentioned in the discussion of  $\Delta H_2^0$  and  $\Delta S_2^0$  it may also be seriously questioned if the basic quasi-lattice assumptions do hold at the attachment of a second  $\text{NO}_2^-$  to  $\text{AgNO}_2$ . Finally it is to be stressed that too much emphasis should not be put on the absolute values of  $a_1$  and  $b_1$  since they are influenced by the choice of  $z$ .

Concluding Remarks. The ability of nitrite ion to form metal complexes in nitrate melts like in aqueous solutions is clearly demonstrated. A definite conclusion about the coordination mode (nitro or nitrito) can not be made, however, until more detailed information is available. The effects of size, charge and chemical character of the central atom of the ligand on the thermodynamics of metal complexation with oxoanions in melts should be known. The previously cited works by Sacchetto and others<sup>17,18</sup> give some insight into these problems and more information is hopefully to be gained from thermodynamic studies of a number of pertinent systems, which are in progress at our laboratory.

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Table I. Review of the experimental material.  $C_{Ag} \approx 1 \times 10^{-3}$  mol kg<sup>-1</sup> in all melts.  $\underline{n}$  = number of melt compositions studied at a given temperature.  $C_O$  and  $(C_{NO_2})_{max}$  are initial and final total concentrations of nitrite.

| T/K | $\underline{n}$ | $C_O \times 10^4 / \text{mol kg}^{-1}$ | $(C_{NO_2})_{max} / \text{mol kg}^{-1}$ |
|-----|-----------------|----------------------------------------|-----------------------------------------|
| 523 | 18              | 3.3                                    | 0.20                                    |
| 538 | 33              | 3.5                                    | 0.16                                    |
| 553 | 18              | 3.7                                    | 0.17                                    |
| 588 | 19              | 4.2                                    | 0.09                                    |
| 623 | 15              | 4.6                                    | 0.09                                    |

Table II. The over-all stability constants  $\beta_i$  for  $Ag^+ - NO_2^-$  complexes in molten 1:1 (K,Na)NO<sub>3</sub>. The limits of error represent 95% confidence limits.

| T/K | $\beta_0$       | $\beta_1 / \text{mol}^{-1} \text{kg}$ | $\beta_2 / \text{mol}^{-2} \text{kg}^2$ |
|-----|-----------------|---------------------------------------|-----------------------------------------|
| 523 | 1.00 $\pm$ 0.02 | 2.9 $\pm$ 0.4                         | 6 $\pm$ 2                               |
| 538 | 1.00 $\pm$ 0.05 | 2.5 $\pm$ 0.5                         | 7 $\pm$ 4                               |
| 553 | 1.00 $\pm$ 0.01 | 2.1 $\pm$ 0.3                         | 11 $\pm$ 1                              |
| 588 | 1.00 $\pm$ 0.01 | 1.7 $\pm$ 0.5                         | 18 $\pm$ 6                              |
| 623 | 1.00 $\pm$ 0.02 | 1.2 $\pm$ 0.8                         | 29 $\pm$ 8                              |

Table III. Estimated standard enthalpy and entropy changes for  $\text{Ag}(\text{NO}_2)_{(1-i)}^{(2-i)} + \text{NO}_2^- \rightarrow \text{Ag}(\text{NO}_2)_i^{(1-i)}$  in 1:1 (K,Na) $\text{NO}_3$  melts, 250-350°C. Stated errors define 95% confidence limits.

| $i$ | $\Delta H_i^\circ / \text{kJ mol}^{-1}$ | $\Delta S_i^\circ / \text{J K}^{-1} \text{mol}^{-1}$ |
|-----|-----------------------------------------|------------------------------------------------------|
| 1   | -23 $\pm$ 2                             | -15 $\pm$ 3                                          |
| 2   | 69 $\pm$ 9                              | 157 $\pm$ 16                                         |

Table IV. Experimental data  $C_{\text{Ag}}$ ,  $C_{\text{NO}_2^-}$ , ( $E_o - E_c$ ) and calculated  $C_{\text{Ag}}/[\text{Ag}^+]$  and  $[\text{NO}_2^-]$  for all investigated melts  $\text{AgNO}_3 - \text{NaNO}_2 - (\text{K,Na})\text{NO}_3$ .

$$T = 523 \text{ K}; \quad C_{\text{Ag}} = 9.84 \times 10^{-4} \text{ mol kg}^{-1}$$

| $\frac{C_{\text{NO}_2^-}}{\text{mol kg}^{-1}}$ | $\frac{E_o - E_c}{\text{mV}}$ | $C_{\text{Ag}}/[\text{Ag}^+]$ | $\frac{[\text{NO}_2^-]}{\text{mol kg}^{-1}}$ |
|------------------------------------------------|-------------------------------|-------------------------------|----------------------------------------------|
| 0.00033                                        | 0                             | 1                             | 0.00033                                      |
| 0.02484                                        | 3.2                           | 1.073                         | 0.02477                                      |
| 0.0500                                         | 6.7                           | 1.160                         | 0.0498                                       |
| 0.0739                                         | 10.0                          | 1.248                         | 0.0737                                       |
| 0.0983                                         | 13.2                          | 1.340                         | 0.0980                                       |
| 0.1234                                         | 16.4                          | 1.439                         | 0.1230                                       |
| 0.1474                                         | 19.6                          | 1.545                         | 0.1470                                       |
| 0.1726                                         | 23.2                          | 1.673                         | 0.1721                                       |
| 0.1973                                         | 26.7                          | 1.808                         | 0.1967                                       |

Table IV, continued.

$$T = 523 \text{ K}; \quad C_{\text{Ag}} = 9.68 \times 10^{-4} \text{ mol kg}^{-1}$$

| $\frac{C_{\text{NO}_2}}{\text{mol kg}^{-1}}$ | $\frac{E_o - E_c}{\text{mV}}$ | $C_{\text{Ag}} / [\text{Ag}^+]$ | $\frac{[\text{NO}_2^-]}{\text{mol kg}^{-1}}$ |
|----------------------------------------------|-------------------------------|---------------------------------|----------------------------------------------|
| 0.00033                                      | 0                             | 1                               | 0.00033                                      |
| 0.02521                                      | 3.2                           | 1.073                           | 0.02514                                      |
| 0.0507                                       | 6.2                           | 1.147                           | 0.0506                                       |
| 0.0759                                       | 9.4                           | 1.231                           | 0.0757                                       |
| 0.1002                                       | 12.6                          | 1.322                           | 0.0999                                       |
| 0.1258                                       | 17.2                          | 1.464                           | 0.1254                                       |
| 0.1505                                       | 19.2                          | 1.530                           | 0.1501                                       |
| 0.1758                                       | 22.4                          | 1.642                           | 0.1753                                       |
| 0.2011                                       | 25.7                          | 1.766                           | 0.2006                                       |

$$T = 538 \text{ K}; \quad C_{\text{Ag}} = 1.020 \times 10^{-3} \text{ mol kg}^{-1}$$

| $\frac{C_{\text{NO}_2}}{\text{mol kg}^{-1}}$ | $\frac{E_o - E_c}{\text{mV}}$ | $C_{\text{Ag}} / [\text{Ag}^+]$ | $\frac{[\text{NO}_2^-]}{\text{mol kg}^{-1}}$ |
|----------------------------------------------|-------------------------------|---------------------------------|----------------------------------------------|
| 0.00035                                      | 0                             | 1                               | 0.00035                                      |
| 0.02269                                      | 3.0                           | 1.066                           | 0.02263                                      |
| 0.04485                                      | 5.8                           | 1.133                           | 0.04472                                      |
| 0.0700                                       | 8.8                           | 1.209                           | 0.0698                                       |
| 0.0894                                       | 11.6                          | 1.284                           | 0.0891                                       |
| 0.1137                                       | 15.1                          | 1.385                           | 0.1134                                       |
| 0.1384                                       | 18.6                          | 1.493                           | 0.1380                                       |

Table IV, continued.

$$T = 538 \text{ K}; \quad C_{\text{Ag}} = 1.024 \times 10^{-3} \text{ mol kg}^{-1}$$

| $\frac{C_{\text{NO}_2}}{\text{mol kg}^{-1}}$ | $\frac{E_{\text{O}} - E_{\text{C}}}{\text{mV}}$ | $C_{\text{Ag}} / [\text{Ag}^+]$ | $\frac{[\text{NO}_2^-]}{\text{mol kg}^{-1}}$ |
|----------------------------------------------|-------------------------------------------------|---------------------------------|----------------------------------------------|
| 0.00035                                      | 0                                               | 1                               | 0.00035                                      |
| 0.02386                                      | 3.2                                             | 1.071                           | 0.02380                                      |
| 0.04513                                      | 5.9                                             | 1.136                           | 0.04500                                      |
| 0.0703                                       | 9.6                                             | 1.230                           | 0.0701                                       |
| 0.0890                                       | 13.5                                            | 1.338                           | 0.0887                                       |

$$T = 538 \text{ K}; \quad C_{\text{Ag}} = 9.71 \times 10^{-4} \text{ mol kg}^{-1}$$

| $\frac{C_{\text{NO}_2}}{\text{mol kg}^{-1}}$ | $\frac{E_{\text{O}} - E_{\text{C}}}{\text{mV}}$ | $C_{\text{Ag}} / [\text{Ag}^+]$ | $\frac{[\text{NO}_2^-]}{\text{mol kg}^{-1}}$ |
|----------------------------------------------|-------------------------------------------------|---------------------------------|----------------------------------------------|
| 0.00035                                      | 0                                               | 1                               | 0.00035                                      |
| 0.02269                                      | 3.2                                             | 1.071                           | 0.02263                                      |
| 0.04525                                      | 6.7                                             | 1.155                           | 0.04513                                      |
| 0.0697                                       | 10.0                                            | 1.241                           | 0.0695                                       |
| 0.0890                                       | 12.4                                            | 1.307                           | 0.0887                                       |
| 0.1135                                       | 15.7                                            | 1.403                           | 0.1132                                       |
| 0.1371                                       | 19.2                                            | 1.513                           | 0.1367                                       |
| 0.1567                                       | 21.5                                            | 1.590                           | 0.1562                                       |

Table IV, continued.

T = 538 K;  $\underline{C}_{Ag} = 1.122 \times 10^{-3} \text{ mol kg}^{-1}$

| $\frac{C_{NO_2}}{\text{mol kg}^{-1}}$ | $\frac{E_O - E_C}{\text{mV}}$ | $\underline{C}_{Ag} / [Ag^+]$ | $\frac{[NO_2^-]}{\text{mol kg}^{-1}}$ |
|---------------------------------------|-------------------------------|-------------------------------|---------------------------------------|
| 0.00035                               | 0                             | 1                             | 0.00035                               |
| 0.02396                               | 2.7                           | 1.060                         | 0.02389                               |
| 0.04630                               | 5.3                           | 1.121                         | 0.04616                               |
| 0.0718                                | 8.2                           | 1.193                         | 0.0716                                |
| 0.0928                                | 10.7                          | 1.260                         | 0.0925                                |
| 0.1178                                | 13.6                          | 1.341                         | 0.1174                                |

T = 538 K;  $\underline{C}_{Ag} = 1.020 \times 10^{-3} \text{ mol kg}^{-1}$

| $\frac{C_{NO_2}}{\text{mol kg}^{-1}}$ | $\frac{E_O - E_C}{\text{mV}}$ | $\underline{C}_{Ag} / [Ag^+]$ | $\frac{[NO_2^-]}{\text{mol kg}^{-1}}$ |
|---------------------------------------|-------------------------------|-------------------------------|---------------------------------------|
| 0.00035                               | 0                             | 1                             | 0.00035                               |
| 0.02304                               | 2.8                           | 1.062                         | 0.02298                               |
| 0.04473                               | 5.4                           | 1.124                         | 0.04460                               |
| 0.0703                                | 8.3                           | 1.196                         | 0.0701                                |
| 0.0903                                | 10.8                          | 1.262                         | 0.0900                                |
| 0.1156                                | 13.8                          | 1.347                         | 0.1152                                |
| 0.1409                                | 18.1                          | 1.477                         | 0.1405                                |

Table IV, continued.

$T = 553 \text{ K}; \quad C_{\text{Ag}} = 9.92 \times 10^{-4} \text{ mol kg}^{-1}$

| $\frac{C_{\text{NO}_2}}{\text{mol kg}^{-1}}$ | $\frac{E_{\text{O}} - E_{\text{C}}}{\text{mV}}$ | $C_{\text{Ag}} / [\text{Ag}^+]$ | $\frac{[\text{NO}_2^-]}{\text{mol kg}^{-1}}$ |
|----------------------------------------------|-------------------------------------------------|---------------------------------|----------------------------------------------|
| 0.00037                                      | 0                                               | 1                               | 0.00037                                      |
| 0.02057                                      | 2.5                                             | 1.054                           | 0.02052                                      |
| 0.04074                                      | 5.0                                             | 1.111                           | 0.04063                                      |
| 0.0657                                       | 8.3                                             | 1.190                           | 0.0655                                       |
| 0.0852                                       | 11.7                                            | 1.278                           | 0.0849                                       |
| 0.1050                                       | 14.4                                            | 1.353                           | 0.1047                                       |
| 0.1240                                       | 16.9                                            | 1.425                           | 0.1236                                       |
| 0.1487                                       | 21.0                                            | 1.553                           | 0.1482                                       |
| 0.1681                                       | 24.1                                            | 1.658                           | 0.1675                                       |

$T = 553 \text{ K}; \quad C_{\text{Ag}} = 1.003 \times 10^{-3} \text{ mol kg}^{-1}$

| $\frac{C_{\text{NO}_2}}{\text{mol kg}^{-1}}$ | $\frac{E_{\text{O}} - E_{\text{C}}}{\text{mV}}$ | $C_{\text{Ag}} / [\text{Ag}^+]$ | $\frac{[\text{NO}_2^-]}{\text{mol kg}^{-1}}$ |
|----------------------------------------------|-------------------------------------------------|---------------------------------|----------------------------------------------|
| 0.00037                                      | 0                                               | 1                               | 0.00037                                      |
| 0.02118                                      | 2.4                                             | 1.052                           | 0.02113                                      |
| 0.04012                                      | 4.9                                             | 1.108                           | 0.04001                                      |
| 0.0637                                       | 7.9                                             | 1.180                           | 0.0635                                       |
| 0.0847                                       | 10.6                                            | 1.249                           | 0.0844                                       |
| 0.1043                                       | 13.7                                            | 1.333                           | 0.1040                                       |
| 0.1228                                       | 17.0                                            | 1.428                           | 0.1224                                       |
| 0.1486                                       | 20.8                                            | 1.547                           | 0.1481                                       |
| 0.1684                                       | 24.8                                            | 1.682                           | 0.1678                                       |

Table IV, continued.

$$T = 588 \text{ K}; \quad C_{\text{Ag}} = 1.044 \times 10^{-3} \text{ mol kg}^{-1}$$

| $\frac{C_{\text{NO}_2}}{\text{mol kg}^{-1}}$ | $\frac{E_{\text{O}} - E_{\text{C}}}{\text{mV}}$ | $C_{\text{Ag}} / [\text{Ag}^+]$ | $\frac{[\text{NO}_2^-]}{\text{mol kg}^{-1}}$ |
|----------------------------------------------|-------------------------------------------------|---------------------------------|----------------------------------------------|
| 0.00042                                      | 0                                               | 1                               | 0.00042                                      |
| 0.02015                                      | 2.0                                             | 1.040                           | 0.02010                                      |
| 0.0399                                       | 5.0                                             | 1.104                           | 0.0398                                       |
| 0.0597                                       | 8.4                                             | 1.180                           | 0.0595                                       |

$$T = 588 \text{ K}; \quad C_{\text{Ag}} = 9.88 \times 10^{-4} \text{ mol kg}^{-1}$$

| $\frac{C_{\text{NO}_2}}{\text{mol kg}^{-1}}$ | $\frac{E_{\text{O}} - E_{\text{C}}}{\text{mV}}$ | $C_{\text{Ag}} / [\text{Ag}^+]$ | $\frac{[\text{NO}_2^-]}{\text{mol kg}^{-1}}$ |
|----------------------------------------------|-------------------------------------------------|---------------------------------|----------------------------------------------|
| 0.00042                                      | 0                                               | 1                               | 0.00042                                      |
| 0.01180                                      | 1.0                                             | 1.020                           | 0.01178                                      |
| 0.02380                                      | 2.0                                             | 1.040                           | 0.02374                                      |
| 0.03531                                      | 3.1                                             | 1.063                           | 0.03521                                      |
| 0.0469                                       | 4.9                                             | 1.102                           | 0.0468                                       |
| 0.0586                                       | 6.8                                             | 1.144                           | 0.0584                                       |
| 0.0709                                       | 9.5                                             | 1.206                           | 0.0706                                       |
| 0.0838                                       | 11.6                                            | 1.257                           | 0.0835                                       |
| 0.0962                                       | 14.4                                            | 1.329                           | 0.0958                                       |

Table IV, continued.

$$T = 588 \text{ K}; \quad \underline{C}_{\text{Ag}} = 9.16 \times 10^{-4} \text{ mol kg}^{-1}$$

| $\frac{\underline{C}_{\text{NO}_2^-}}{\text{mol kg}^{-1}}$ | $\frac{E_{\text{O}} - E_{\text{C}}}{\text{mV}}$ | $\underline{C}_{\text{Ag}} / [\text{Ag}^+]$ | $\frac{[\text{NO}_2^-]}{\text{mol kg}^{-1}}$ |
|------------------------------------------------------------|-------------------------------------------------|---------------------------------------------|----------------------------------------------|
| 0.00042                                                    | 0                                               | 1                                           | 0.00042                                      |
| 0.01171                                                    | 0.8                                             | 1.016                                       | 0.01169                                      |
| 0.02350                                                    | 2.4                                             | 1.048                                       | 0.02345                                      |
| 0.03542                                                    | 4.1                                             | 1.084                                       | 0.03533                                      |
| 0.0473                                                     | 5.9                                             | 1.124                                       | 0.0472                                       |
| 0.0588                                                     | 8.5                                             | 1.183                                       | 0.0586                                       |

$$T = 623 \text{ K}; \quad \underline{C}_{\text{Ag}} = 1.048 \times 10^{-3} \text{ mol kg}^{-1}$$

| $\frac{\underline{C}_{\text{NO}_2^-}}{\text{mol kg}^{-1}}$ | $\frac{E_{\text{O}} - E_{\text{C}}}{\text{mV}}$ | $\underline{C}_{\text{Ag}} / [\text{Ag}^+]$ | $\frac{[\text{NO}_2^-]}{\text{mol kg}^{-1}}$ |
|------------------------------------------------------------|-------------------------------------------------|---------------------------------------------|----------------------------------------------|
| 0.00046                                                    | 0                                               | 1                                           | 0.00046                                      |
| 0.01527                                                    | 1.4                                             | 1.026                                       | 0.01524                                      |
| 0.02517                                                    | 2.7                                             | 1.052                                       | 0.02510                                      |
| 0.04094                                                    | 4.6                                             | 1.092                                       | 0.04080                                      |
| 0.0518                                                     | 7.4                                             | 1.148                                       | 0.0516                                       |
| 0.0665                                                     | 10.0                                            | 1.205                                       | 0.0662                                       |
| 0.0821                                                     | 13.0                                            | 1.274                                       | 0.0817                                       |

Table IV, continued.

$$T = 623 \text{ K}; \quad \underline{C}_{\text{Ag}} = 1.004 \times 10^{-3} \text{ mol kg}^{-1}$$

| $\frac{\underline{C}_{\text{NO}_2}}{\text{mol kg}^{-1}}$ | $\frac{E_{\text{O}} - E_{\text{C}}}{\text{mV}}$ | $\underline{C}_{\text{Ag}} / [\text{Ag}^+]$ | $\frac{[\text{NO}_2^-]}{\text{mol kg}^{-1}}$ |
|----------------------------------------------------------|-------------------------------------------------|---------------------------------------------|----------------------------------------------|
| 0.00046                                                  | 0                                               | 1                                           | 0.00046                                      |
| 0.01564                                                  | 1.1                                             | 1.019                                       | 0.01561                                      |
| 0.02528                                                  | 2.6                                             | 1.050                                       | 0.02522                                      |
| 0.04126                                                  | 5.4                                             | 1.106                                       | 0.04112                                      |
| 0.0524                                                   | 7.9                                             | 1.158                                       | 0.0522                                       |
| 0.0672                                                   | 10.4                                            | 1.214                                       | 0.0669                                       |
| 0.0823                                                   | 13.0                                            | 1.274                                       | 0.0819                                       |
| 0.0922                                                   | 17.6                                            | 1.388                                       | 0.0918                                       |

### Figure captions

Figure 1.  $C_{Ag}/[Ag^+]$  versus  $[NO_2^-]$  in molten 1:1 (K,Na)NO<sub>3</sub> at 553 K. Filled and unfilled symbols represent duplicate runs.

Figure 2. The fraction  $\alpha$  of Ag(I) present in different species in 1:1 (K,Na)NO<sub>3</sub> at 523 K and 623 K as a function of the nitrite concentration in the melts. The curves - calculated from the constants of Table II - are extended over the  $[NO_2^-]$  range experimentally covered at the two extreme temperatures.

Figure 3. Plots of  $-\Delta G_1^0$  for reactions (10) and (11) versus T. The equations of the solid lines are defined by the parameters of Table III.

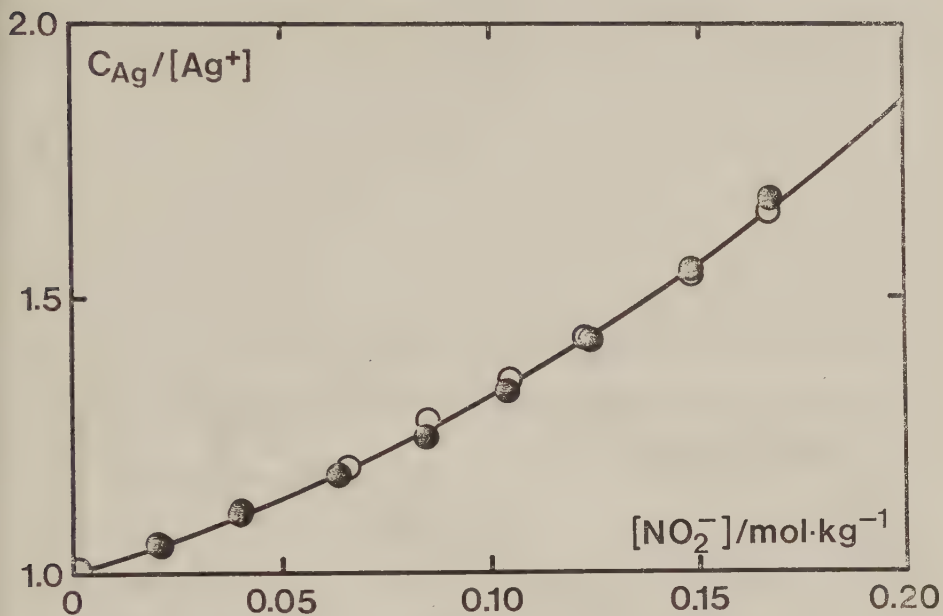


Figure 1.

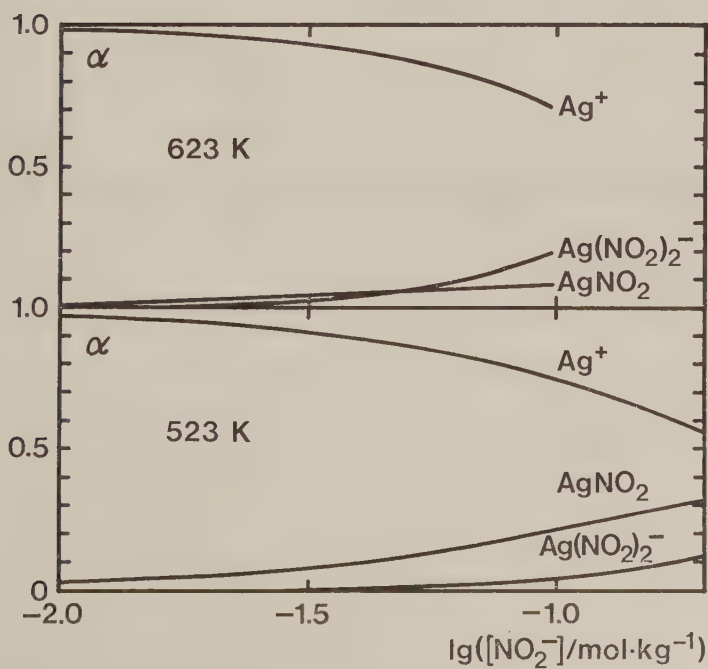


Figure 2.

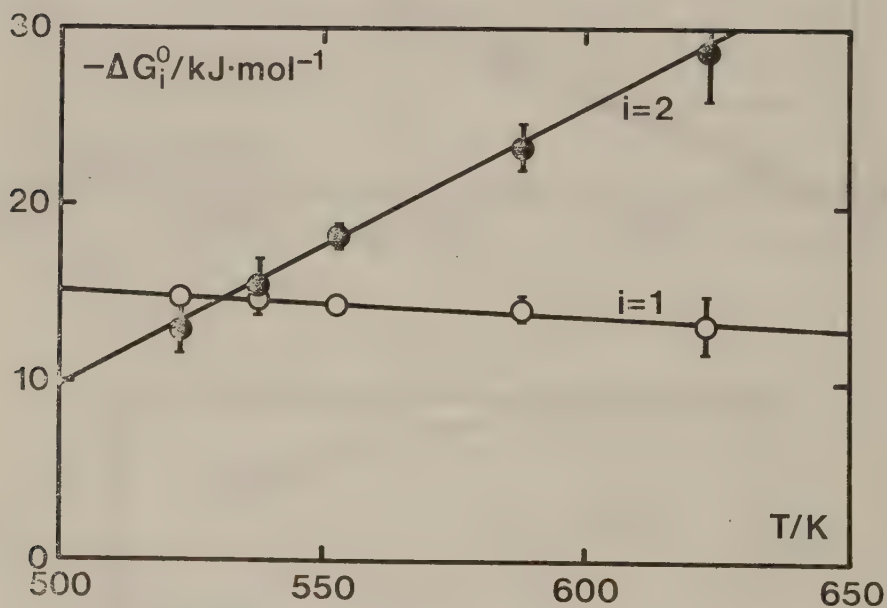


Figure 3.

Thermodynamics of Solid Solutions (Ag,Na)IO<sub>3</sub> and Silver Iodate Complexation in Molten (K,Na)NO<sub>3</sub>. A Potentiometric and Solubility Study.

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Complex formation between Ag(I) and IO<sub>3</sub><sup>-</sup> in equimolar

(K,Na)NO<sub>3</sub> has been studied by emf measurements at five temperatures between 523 and 623 K and by solubility measurements at 553 K. Solid solutions (Ag, Na)IO<sub>3</sub>, exhibiting positive deviations from thermodynamic ideality, are formed when AgIO<sub>3</sub> is equilibrated with melts rich in iodate, and a transition to a new phase with  $x_{\text{NaIO}_3} = 0,38 \pm 0,01$  is detected by thermodynamic methods and by X-ray powder diffraction analysis. All data can be rationalized by a model of stepwise formation of complexes AgIO<sub>3</sub>, Ag(IO<sub>3</sub>)<sub>2</sub><sup>-</sup> and Ag<sub>2</sub>IO<sub>3</sub><sup>+</sup>.  $\Delta H_1^{\circ}$  and  $\Delta S_1^{\circ}$  for the process  $\text{Ag}^+ + \text{IO}_3^- \rightarrow \text{AgIO}_3$  have been estimated from the temperature dependence of the stability constant  $\beta_{11}$  for AgIO<sub>3</sub>. The reaction is slightly endothermic and the entropy gain is responsible for the thermodynamic stability of AgIO<sub>3</sub>. A critical comparison of  $\Delta S_1^{\circ}$  with predictions from the quasi-lattice theory is made.

## Introduction

This paper is part of a series of oxoanion-silver(I) complexation studies in molten equimolar  $(K,Na)NO_3$  aiming at a rationalization of the influence of parameters such as ionic size, charge and nature of the central atom of the oxoanion on the thermodynamics of the complexation. Ag(I) association with a number of divalent oxoanions in various molten nitrates has been studied by different authors.<sup>1</sup> In these works the pair association energy of the quasi-lattice theory is calculated for the 1:1 association processes, and its temperature dependence or independence is discussed. So far, however, monovalent oxoanions have received little attention as ligands in ionic melts. We have recently given results from a study of the Ag(I)-nitrite system in 1:1  $(K,Na)NO_3$ ,<sup>2</sup> and ionic association between  $IO_3^-$  and  $Ca^{2+}$  in the same solvent has been considered by Holmberg.<sup>3</sup>

The iodate ion is an attractive ligand in molten nitrate solvents since it has approximately the same size, although different geometry, and the same ionic charge as the solvent nitrate ion. These properties delete entropy contributions from configurational changes as ions of higher charge are introduced into a melt of monovalent ions only.

Habboush and Kerridge found the iodate ion to be stable up to 500°C in  $(K,Li)NO_3$ . The nitrite formed by thermal decomposition of nitrate was said to reduce  $IO_3^-$  to a measurable extent above this temperature.<sup>4</sup> According to Sacchetto and

coworkers<sup>5</sup>  $\text{IO}_3^-$  is unstable in unspecified nitrate melts containing  $\text{Ag(I)}$ . Precipitation of  $\text{AgI}$  was observed and the presence of  $\text{Ag(I)}$  is thus expected to facilitate the iodate decomposition. We have paid special attention to this problem by studying separately the thermal stability of  $\text{IO}_3^-$  in  $(\text{K,Na})\text{NO}_3 - \text{AgNO}_3$  melts in the range 250 - 350°C.

Two independent methods, emf and solubility measurements, have been used to investigate the  $\text{Ag(I)}$ -iodate complexation. Emf measurements were performed with silver(I) concentration cells at various temperatures in an interval of 100 K, while the solubility study was made at one reference temperature, 280°C.

It was observed in preliminary experiments that alkali metal iodate is dissolved into  $\text{AgIO}_3$  when the solid was equilibrated with melts rich in iodate. This tendency of the highly concentrated ions of the solvent to replace ions in the solid phase appears to be a much more frequent problem in solubility studies of complex formation in ionic melts than in similar studies involving molecular solvents at ambient temperatures. Nevertheless solubility data can be used to determine stability constants for complex ions by means of a simultaneous thermodynamic treatment of all heterogeneous and homogenous equilibria considered. This calculation method has been outlined previously by Holmberg.<sup>6</sup>

## Experimental section

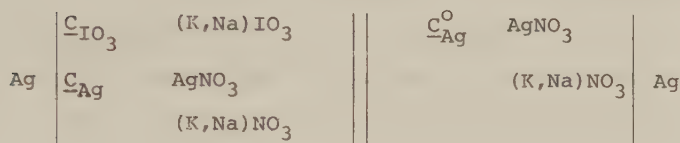
Silver nitrate, sodium nitrate and potassium nitrate (Merck p.a.) were pretreated and stored as described previously.<sup>7</sup> Alkali metal iodate was added as an equimolar mixture of sodium iodate and potassium iodate (Merck p.a.) These salts were dried separately, ground together and then dried again at 120°C for several days prior to use. Silver iodate was either preparations made by us from  $\text{AgNO}_3$  and  $\text{NaIO}_3$  or commercial preparation from BDH Chemicals Ltd. In some cases silver iodate was precipitated directly in the melt from added alkali iodate and silver nitrate.

Furnaces, temperature control and measurement and the construction of the cell for emf measurements have been described elsewhere.<sup>2,7,8</sup>

Solubility Measurements. Systems with approximately 1 g of  $\text{AgIO}_3$ , 75 g  $(\text{K,Na})\text{NO}_3$  and varying amounts of  $\text{AgNO}_3$  or  $(\text{K,Na})\text{IO}_3$  were agitated for at least 50 h in Pyrex glass tubes (series A). Maximum concentrations were  $1.0 \text{ mol kg}^{-1}$   $\text{AgNO}_3$  and  $0.8 \text{ mol kg}^{-1}$   $(\text{K,Na})\text{IO}_3$ . Samples from the nitrate phase were analysed for silver and iodate. Total iodate was determined by the conventional iodometric procedure using sodium thiosulphate solutions, standardized against potassium iodate. Silver was determined by electroanalytical precipitation of Ag on a rotating platinum cathode from hot aqueous cyanide solutions. In a separate series (B) 10 g  $\text{AgIO}_3$  was used in order to make it possible to calculate the composition of the solid from the difference between added and found amounts of various ions in the nitrate melt after

equilibration.

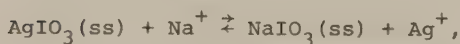
Emf Measurements. The following cell was used:



The cell was usually set up with 250 g  $(\text{K,Na})\text{NO}_3$  and  $0.003 \text{ mol kg}^{-1} \text{ AgNO}_3$  in both cell compartments and left with vigorous stirring for about 18 hours. Successive additions of  $(\text{K,Na})\text{IO}_3$  were then made and the emf was measured repeatedly at constant temperature over four different electrode combinations after each addition by means of a Digiscan 10 PRC datalogging unit from Mess+System Technik, München. The E-values were measured to  $\pm 0.05 \text{ mV}$ . Stable readings were as a rule obtained within 30 min. after each addition of iodate. In order to decide whether polynuclear species are present or not in melts with an excess of iodate over silver, some series were run with  $\underline{C}_{\text{Ag}} = 0.001$  and  $0.03 \text{ mol kg}^{-1}$  as well. Eight different compositions were as a rule studied in every series; maximum concentration of iodate was  $0.3 \text{ mol kg}^{-1}$ . All series of measurements were duplicated at least once. Data were recorded at five different temperatures in the range  $250 - 350^\circ\text{C}$ .

The Stability of Iodate. The solubility of iodate is larger than  $1.3 \text{ mol kg}^{-1}$  at  $280^\circ\text{C}$  when added as a 1:1 mixture of  $\text{KIO}_3$  and  $\text{NaIO}_3$  to the pure  $(\text{K,Na})\text{NO}_3$  solvent. The thermal stability was checked in a number of melts listed in Table I.

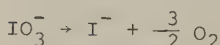
Decomposition of  $\text{IO}_3^-$  does not occur in pure  $(\text{K},\text{Na})\text{NO}_3$  according to the analyses of melt A made after several days at  $280^\circ\text{C}$ . Melt B was high in iodate and rather low in silver concentration to avoid precipitation of  $\text{AgIO}_3$ . It was made to check if the observed difference between added and found iodate contents in the melts equilibrated with solid  $\text{AgIO}_3$ , which we have attributed to the ion exchange reaction



might in part be due to iodate decomposition. No changes were found within 50 h, the normal running time for systems used in solubility studies.

As it has been claimed<sup>5</sup> that  $\text{IO}_3^-$  is unstable in nitrate melts containing  $\text{Ag}(\text{I})$ , melt C with even higher silver content was studied. No variation in  $\underline{\text{C}}_{\text{IO}_3}$  with time could be detected and no precipitation of  $\text{AgI}$  was observed. Melt D was prepared with an iodate concentration corresponding to the largest one used in the emf measurements and was equilibrated at the highest temperature used. The iodate concentration in this melt remained constant for at least five hours, which is more than the normal time for one emf titration series.

It is thus safely concluded that the reaction



does not occur to any measurable extent under the conditions used in the present study up to 350°C.

### EMF Measurements

Stability constant, defined by

$$\beta_{mn} = \frac{[Ag_m(IO_3)_n]^{m-n}}{[Ag^+]^m [IO_3^-]^n} \quad (1)$$

were determined by use of the stoichiometric requirement

$$C_{Ag} = [Ag^+] + \sum_m \sum_n m [Ag_m(IO_3)_n]^{m-n} \quad (2)$$

Since junction potentials are negligible in these dilute ionic melts, it holds

$$\Delta E = \frac{R}{F} \ln (C_{Ag} / [Ag^+]) \quad (3)$$

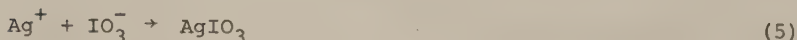
where  $\Delta E$  is the emf at the iodate concentration considered minus the emf at  $C_{IO_3} = 0$  in the left hand compartment of the cell. Combination of eqns. (1)-(3) yields

$$\exp\left(\frac{\Delta E \cdot F}{R T}\right) = 1 + \sum_m \sum_n m \beta_{mn} [Ag^+]^{m-1} [IO_3^-]^n \quad (4)$$

It appeared that the left hand member of the eqn. (4) could be accurately described by a second degree polynomial in  $[\text{IO}_3^-]$  independent of the  $\text{Ag(I)}$  content of the melts. Hence, the complexes  $\text{AgIO}_3$  and  $\text{Ag}(\text{IO}_3)_2^-$  are the only species that have to be considered in melts having iodate in excess over silver. This is exemplified by Fig. 1, displaying results from three series of measurements at  $280^\circ\text{C}$ .

The final treatment of data was made by use of a computer program yielding the best fitting parameters  $\beta_{m,n}$  from eqn. (4) by minimizing the sum of squared errors  $(\Delta E_{\text{obs}} - \Delta E_{\text{calc}})^2$ . Table II gives stability constants from the emf measurements at five different temperatures. As can be seen from the Table the data recorded at 622K did not permit any meaningful estimate of  $\beta_{12}$  at this temperature. This is obviously due to the fact that the stability of  $\text{Ag}(\text{IO}_3)_2^-$  decreases rapidly with increasing  $T$ .

The thermodynamic parameters  $\Delta H_1^0$  and  $\Delta S_1^0$  for the first step of complexation, schematically written as



have been estimated from a study of  $\Delta G_1^0 = -R T \ln \beta_{11}$

as a function of temperature. The standard state chosen relates to unity ionic fractions.  $\Delta G_1^0$  is a good linear function of  $T$  so  $\Delta H_1^0$  and  $\Delta S_1^0$  have been estimated by linear regression analysis. In doing so every data point was given an individual weight proportional to  $(\sigma_1(T))^{-2}$ ,

where  $\underline{\sigma}_1(\underline{T})$  is given by eqn. (6):

$$\underline{\sigma}_1(\underline{T}) = \underline{R} \underline{T} \frac{\underline{\sigma}(\underline{\beta}_{11})}{\underline{\beta}_{11}} \quad (6)$$

Here  $\underline{\sigma}(\underline{\beta}_{11})$  is the estimated standard deviation in  $\underline{\beta}_{11}$  at the temperature in question. Resulting parameters are

$$\Delta \underline{H}_1^{\circ} = (2.3 \pm 1.6) \text{ kJ mol}^{-1} \text{ and } \Delta \underline{S}_1^{\circ} = (31 \pm 3) \text{ J K}^{-1} \text{ mol}^{-1}.$$

Stated errors are one estimated standard deviation.

Data for the second step of complexation are not accurate enough to make a similar estimate of  $\Delta \underline{H}_2^{\circ}$  and  $\Delta \underline{S}_2^{\circ}$  meaningful.

### Solubility Measurements

The solid phase. The results from series B clearly indicate that silver ions of the solid phase are partially replaced by alkali metal ions from the melt in systems with  $\underline{C}_{\text{IO}_3} > \underline{C}_{\text{Ag}}$ . In order to decide whether  $\text{Na}^+$ ,  $\text{K}^+$  or both are involved in the ion exchange reaction, melts with pure  $\text{KNO}_3$  and pure  $\text{NaNO}_3$  as solvents were prepared with  $1.2 \text{ mol kg}^{-1} \text{ KIO}_3$  and  $\text{NaIO}_3$  respectively and were equilibrated with solid  $\text{AgIO}_3$  at  $350^\circ\text{C}$ . The mole fraction of  $\text{AgIO}_3$ ,  $\underline{x}_1$ , in the solid phase after equilibration was 0.52 in the sodium system and 0.96 in the potassium system, indicating that sodium is respon-

sible for the paramount part of the ion exchange.

$\underline{x}_2 (=1-\underline{x}_1)$  raises slowly as  $\underline{C}_{\text{IO}_3}$  is increased from 0 to 0.65 mol kg<sup>-1</sup>. Here  $\underline{x}_2$  increases very steeply to  $0.38 \pm 0.01$ , indicating a phase transition. After this point  $\underline{x}_2$  of the new "Na-rich" phase increases slowly with  $\underline{C}_{\text{IO}_3}$  again. Fig. 2 gives the composition of the solid as a function of  $\underline{C}_{\text{IO}_3}$  in the melt.

X-ray powder diffraction studies were made at room temperature on solids with  $\underline{x}_2=0.06, 0.18, 0.29$  and  $0.40$  as well as pure  $\text{AgIO}_3$  and  $\text{NaIO}_3$ . The diffraction patterns for  $\underline{x}_2=0.06$  and for pure  $\text{AgIO}_3$  were identical. New lines, different from those of  $\text{NaIO}_3$ , appeared for the next two powders,  $\underline{x}_2=0.18$  and  $0.29$ . For  $\underline{x}_2=0.40$  the lines typical of  $\text{AgIO}_3$  had disappeared. The half-filled symbols of Fig. 2 thus represent systems with formal values of  $\underline{x}_2$  corresponding to mixtures of two solid solutions with different crystal structures.

The diffraction pattern of the new Na-rich phase could be properly indexed on the basis of an orthorhombic symmetry like  $\text{AgIO}_3$ <sup>9</sup> and  $\text{NaIO}_3$ <sup>10</sup>. Cell parameters for  $\underline{x}_2=0.40$  are  $\underline{a}=6.801(4)\text{\AA}$ ,  $\underline{b}=12.29(1)\text{\AA}$  and  $\underline{c}=6.127(3)\text{\AA}$ . It is to be noted that  $\underline{b}$  falls very close to the weighted average of the corresponding edge lengths for  $\text{AgIO}_3$  ( $15.13\text{\AA}$ ) and  $\text{NaIO}_3$  ( $8.10\text{\AA}$ ) which is  $12.32\text{\AA}$ , whereas no similar relation is found for  $\underline{a}$  and  $\underline{c}$ .

The activity,  $\underline{a}_1$ , of  $\text{AgIO}_3$  in the solid phase, has to be known in order that solubility data may be used for the de-

termination of complex ion stabilities.  $\underline{a}_1$  is computed from

$$\underline{a}_{1j} = \exp \left[ \frac{\ln \underline{R}}{\ln \underline{R}_0} \int_{\ln \underline{R}_0}^j (\underline{x}_2/\underline{x}_1) d \ln \underline{R} \right] \quad (7)$$

where  $\underline{R} = (\underline{Y} \cdot [\text{IO}_3^-])^{-1}$  and  $\underline{Y} = [\text{Na}^+]/([\text{Na}^+] + [\text{K}^+])$ ,<sup>6</sup>  
 The index  $j$  is used to denote different quantities referring to the same actual system and  $\underline{R}_0$  refers to a system with  $\underline{x}_1=1$  and  $\underline{a}_1=1$  i.e. the standard state chosen for  $\text{AgIO}_3$ . Hence, the activity of  $\text{AgIO}_3$  in the Na-rich phase also relates to pure  $\text{AgIO}_3$ . Fig. 3 gives  $\underline{a}_1$  as a function of  $\underline{x}_1$  in the two solid phases. Both kinds of solid solutions exhibit positive deviations from thermodynamic ideality.

Solubility Measurements,  $\frac{C_{\text{IO}_3}}{C_{\text{Ag}}} > \frac{C_{\text{IO}_3}}{C_{\text{Ag}}}$ . Fig. 4 surveys the experimental material of series A.

It was observed that solubilities, determined in series B were - to a small but significant extent - higher than the corresponding values obtained in series A. This difference can be attributed to the shift in the K:Na ratio of the nitrate melt brought about by the selective Ag-Na exchange reaction between the melt and the solid. Data from series A only were used in the determination of complex stabilities. In this way it was ensured that stability constants determined by emf and solubility methods refer to as similar cation composition of the solvent as possible. Values of  $\underline{x}_1$  and  $\underline{a}_1$  were transferred from series

B to series A by means of interpolation in plots of  $\underline{x}_1$  and  $\underline{a}_1$  versus  $\underline{y}$   $[\text{IO}_3^-]$ .

A general expression for the solubility "product" of  $\text{AgIO}_3$  is

$$\underline{K}_S = [\text{Ag}^+][\text{IO}_3^-]/\underline{a}_1 \quad (8)$$

By combination with eqns. (1) and (2):

$$\underline{C}_{\text{Ag}}[\text{IO}_3^-] \underline{a}_1^{-1} = \underline{K}_S (1 + \sum_{\underline{m}} \sum_{\underline{n}} \underline{\beta}_{\underline{m} \underline{n}} [\text{Ag}^+]^{\underline{m}-1} [\text{IO}_3^-]^{\underline{n}}) \quad (9)$$

Inspection of the solubility curve shows that no species with more negative formal ionic charge than -1 are formed. Since emf measurements clearly show the absence of polynuclear complexes in this composition range, all data were treated according to eqn. (9) assuming  $\text{AgIO}_3$  and  $\text{Ag}(\text{IO}_3)_2^-$  only. A second degree polynomial in  $[\text{IO}_3^-]$  that describes the experimental data  $\underline{C}_{\text{Ag}}[\text{IO}_3^-] \underline{a}_1^{-1}$  can easily be found by iteration.  $\underline{K}_S$ ,  $\underline{K}_S \underline{\beta}_{11}$  and  $\underline{K}_S \underline{\beta}_{12}$  are thus determined.

Solubility measurements,  $\underline{C}_{\text{Ag}} > \underline{C}_{\text{IO}_3}$ . In analogy with eqn. (9) we have

$$\underline{C}_{\text{IO}_3} [\text{Ag}^+] \underline{a}_1^{-1} = \underline{K}_S (1 + \sum_{\underline{m}} \sum_{\underline{n}} \underline{\beta}_{\underline{m} \underline{n}} [\text{Ag}^+]^{\underline{m}} [\text{IO}_3^-]^{\underline{n}-1}) \quad (10)$$

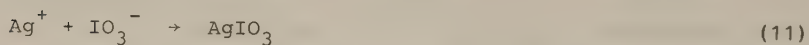
where  $\underline{a}_1$  can be set to unity as the solid phase is pure  $\text{AgIO}_3$  in all systems where  $\text{Ag(I)}$  is in excess over iodate in the melt. From the shape of the solubility curve it is

clear that complex ions of a formal charge +1 have to be taken into account in a proper description model. Any complex of the composition  $\text{Ag}_{\underline{m}}(\text{IO}_3)_{\underline{m}-1}^+$  may be considered but we have made the reasonable assumption that the simplest complex  $\text{Ag}_2\text{IO}_3^+$  is formed. The experimental data  $\underline{C}_{\text{IO}_3} [\text{Ag}^+]$  is well described by a second degree polynomial in  $[\text{Ag}^+]$ , employing an iterative least squares calculation process that yields  $\underline{K}_s$ ,  $\underline{K}_s\beta_{11}$  and  $\underline{K}_s\beta_{21}$  at 280 °C.

### Discussion

From aqueous solution chemistry the complexes  $\text{AgIO}_3$  and  $\text{Ag}(\text{IO}_3)_2^-$  are well characterized<sup>11</sup> and even cationic complexes have been proposed.<sup>12</sup> These are the same species as we have found in nitrate melts although the association does not by far proceed to the same extent in the ionic liquid. Table III displays a comparison between stability constants and  $\underline{K}_s$  determined by different methods at 280 °C. The results from solubility and emf measurements agree very well within the estimated limits of error. It is clear, though, that emf measurements give the most precise estimate of  $\beta_{11}$ . Fig. 5 shows the fraction  $\underline{\alpha}$  of the different silvercontaining species as a function of  $[\text{IO}_3^-]$  at 524 K and at 588 K.  $\text{Ag}^+$  and  $\text{AgIO}_3$  are the dominating species containing silver(I), and  $\text{Ag}(\text{IO}_3)_2^-$  contributes at most to only 16 % of  $\underline{C}_{\text{Ag}}$  at 524 K. This fraction decreases rapidly with increasing  $\underline{T}$ , making  $\text{Ag}(\text{IO}_3)_2^-$  practically undetectable at 622 K.

The enthalpy change for the first step of ionic association



does not differ significantly from zero. This is about the expected value if only changes in electrostatic interactions between hard-sphere ions are considered in a model where process (11) is more rigorously treated as a 1:1 exchange of  $\text{NO}_3^-$  for  $\text{IO}_3^-$  between two different quasi-static cationic environments.<sup>3</sup> The thermodynamic stability of  $\text{AgIO}_3$  is thus exclusively due to a comparably large entropy gain on association of  $\text{Ag}^+$  with  $\text{IO}_3^-$ .

A comparison between  $\text{IO}_3^-$  and  $\text{NO}_2^-$ <sup>2</sup> as ligands for  $\text{Ag}^+$  in molten  $(\text{K},\text{Na})\text{NO}_3$  is instructive, since both ligands are monovalent polyatomic oxoanions. Although the stability constants for the 1:1 complexes, and hence  $\Delta G_1^0$ , are almost identical at the reference temperature 280 °C, the  $\Delta H_1^0$  and  $\Delta S_1^0$  patterns are quite different. The nitrite association is favoured by a large negative  $\Delta H_1^0$  term but disfavoured by a substantial loss of entropy. This suggests that a schematic description of the association, such as (11), may represent quite different kinds of processes on the molecular level even in cases of total ionic charge equality.

The question therefore arises if straightforward applications of lattice-like models are always justified. We calculated the specific pair association energy  $\Delta A_1$  for process (11) at five different temperatures using the general quasi-lattice theory

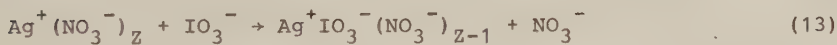
of Blander.<sup>14</sup> The lattice coordination number  $\underline{Z}$  was set to 5 in order to conform to previous calculations by Sachetto and coworkers.<sup>1,5,13</sup>

As  $\Delta \underline{S}_1^{\circ}$  indicates,  $\Delta \underline{A}_1$  has a considerable temperature dependence, which can be generalized as

$$\Delta \underline{A}_1 = \underline{a} + \underline{b} \cdot T \quad (12)$$

since  $\partial(\Delta \underline{A}_1)/\partial T$  is virtually temperature independent. Linear regression yields  $\underline{a} = (1.7 \pm 0.6) \text{ kJ mol}^{-1}$  and  $\underline{b} = (-18 \pm 1) \text{ J K}^{-1} \text{ mol}^{-1}$ . The parameters refer to the same standard state as  $\Delta \underline{H}_1^{\circ}$  and  $\Delta \underline{S}_1^{\circ}$  and are given within 95 % confidence limits.

Substantial values of  $\underline{b}$  have previously been attributed to entropy effects due to changes in internal degrees of freedom for polyatomic solute and solvent ions<sup>1</sup> taking part in processes such as



The internal entropy change,  $\Delta \underline{S}_{\text{int}}^{\circ}$ , may be roughly estimated, however, from vibrational spectra of  $\text{IO}_3^-$  and  $\text{NO}_3^-$  in various cationic environments and from the reasonable assumption that the entropy effects of restrictions on the rotation in the (K,Na) and (Ag,K,Na) environments are related to the products of principal moments of inertia in essentially the same way for  $\text{NO}_3^-$  and  $\text{IO}_3^-$ .  $\Delta \underline{S}_{\text{int}}^{\circ}$  should thus probably fall between -2 and  $-18 \text{ J K}^{-1} \text{ mol}^{-1}$ , which gives a configurational

contribution  $\Delta \underline{S}_{\text{Conf}}^{\text{O}} = (41 \pm 11) \text{ J K}^{-1} \text{ mol}^{-1}$ . Despite the large uncertainty in these figures, they clearly show that the ideal value of the quasi-lattice model,  $\Delta \underline{S}_{\text{Conf}}^{\text{O}} = (14 \pm 3) \text{ J K}^{-1} \text{ mol}^{-1}$  (for reasonable values of  $\underline{z}$  around 5), is not obtained, which rules out the "internal entropy explanation" to  $\partial(\Delta \underline{A}_1)/\partial \underline{T}$ .

The negative sign of  $\underline{b}$  is at least in qualitative agreement with the prediction by Bombi and Sacchetto<sup>13</sup> of the temperature dependence of  $\Delta \underline{A}_1$ , which is entirely attributed to a non-random distribution of solvent cations in a mixed solvent system. The magnitude, however, would require an unrealistically large difference between  $\Delta \underline{A}_1$  in pure  $\text{NaNO}_3$  and pure  $\text{KNO}_3$  in order to be accounted for in this way. In our opinion the apparent temperature dependence of  $\Delta \underline{A}_1$  is largely due to configurational entropy contributions in excess of those predicted by the quasi-lattice model.

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Supplementary Material Available: Tables IV-VI, giving all experimental data from solubility and emf measurements (10 pages). Ordering information is given on any current masthead page.

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Table I. Tests of the iodate stability in equimolar (K,Na)NO<sub>3</sub>. Melt compositions and results from iodate analyses made after various time intervals.

| Melt t/°C | From weighed in amounts                 |                                           | Analytical results                                |                 |
|-----------|-----------------------------------------|-------------------------------------------|---------------------------------------------------|-----------------|
|           | $\underline{C}_{Ag}/\text{mol kg}^{-1}$ | $\underline{C}_{IO_3}/\text{mol kg}^{-1}$ | time/h; $\underline{C}_{IO_3}/\text{mol kg}^{-1}$ |                 |
| A 280     | -                                       | 0.1034                                    | 24;0.1031<br>96;0.1030                            | 48;0.1031       |
| B 280     | 0.026                                   | 0.803                                     | 25;0.805                                          | 50;0.807        |
| C 280     | 0.100                                   | 0.0584                                    | 24;0.0579<br>72;0.0579                            | 48;0.0584       |
| D 350     | 0.029                                   | 0.302                                     | 1;0.301                                           | 3;0.302 5;0.301 |

Table II. The over-all stability constants  $\beta_{11}$  and  $\beta_{12}$  for Ag<sup>+</sup>-IO<sub>3</sub><sup>-</sup> complexes in molten 1:1 (K,Na)NO<sub>3</sub> from emf measurements. The limits of error are 95 % confidence limits.

| T/K | $\beta_{11}/\text{mol}^{-1} \text{ kg}$ | $\beta_{12}/\text{mol}^{-2} \text{ kg}^2$ |
|-----|-----------------------------------------|-------------------------------------------|
| 524 | 2.27±0.12                               | 3.7±0.6                                   |
| 538 | 2.26±0.15                               | 2.0±0.7                                   |
| 553 | 2.28±0.14                               | 2.4±0.7                                   |
| 588 | 2.34±0.15                               | 1.4±0.7                                   |
| 622 | 2.43±0.07                               | -                                         |

Table III. Stability constants and  $K_s$  for  $\text{AgIO}_3$  in 1:1  
 $(\text{K,Na})\text{NO}_3$  at  $280^\circ\text{C}$  determined by different experimental  
methods. The errors are 95 % confidence limits.

| $K_s \times 10^3 / \text{mol}^2 \text{ kg}^{-2}$ | $\beta_{11} / \text{mol}^{-1} \text{ kg}$ | $\beta_{12} / \text{mol}^{-2} \text{ kg}^2$ | $\beta_{21} / \text{mol}^{-2} \text{ kg}^2$ | Method                                 |
|--------------------------------------------------|-------------------------------------------|---------------------------------------------|---------------------------------------------|----------------------------------------|
| $10 \pm 2$                                       | $3.5 \pm 1.0$                             | -                                           | $2.1 \pm 1.0$                               | sol. $C_{\text{Ag}} > C_{\text{IO}_3}$ |
| $10 \pm 1$                                       | $2.1 \pm 0.7$                             | $2.2 \pm 0.8$                               | -                                           | sol. $C_{\text{IO}_3} > C_{\text{Ag}}$ |
| -                                                | $2.3 \pm 0.1$                             | $2.4 \pm 0.7$                               | -                                           | emf                                    |

Table IV. Experimental solubility data from series B.  $x_1$  and  
 $a_1$  are determined as described in the text.

| $C_{\text{Ag}} / \text{mol kg}^{-1}$ | $C_{\text{IO}_3} / \text{mol kg}^{-1}$ | $x_1$ | $a_1$ |
|--------------------------------------|----------------------------------------|-------|-------|
| 0.1020                               | 0.193                                  | 0.983 | 1.000 |
| 0.0650                               | 0.261                                  | 1.004 | 1.000 |
| 0.0661                               | 0.370                                  | 0.953 | 0.996 |
| 0.0591                               | 0.487                                  | 0.941 | 0.979 |
| 0.0572                               | 0.600                                  | 0.907 | 0.964 |
| 0.0552                               | 0.649                                  | 0.658 | -     |
| 0.0582                               | 0.651                                  | 0.707 | -     |
| 0.0508                               | 0.666                                  | 0.614 | 0.898 |
| 0.0522                               | 0.706                                  | 0.600 | 0.889 |
| 0.0508                               | 0.743                                  | 0.601 | 0.858 |
| 0.0526                               | 0.748                                  | 0.603 | 0.870 |
| 0.0505                               | 0.845                                  | 0.579 | 0.808 |

Table V. Experimental solubility data from series A.  $K_s$  is computed from  $[Ag^+]$  and  $[IO_3^-]$  (as calculated from the stability constants of Table III) and the activities from column four.

| $C_{IO_3}/\text{mol kg}^{-1}$ | $C_{Ag}/\text{mol kg}^{-1}$ | $x_1$ | $a_1$ | $K_s/\text{mol}^2\text{kg}^{-2}$ |
|-------------------------------|-----------------------------|-------|-------|----------------------------------|
| 0.793                         | 0.0429                      | 0.59  | 0.832 | 0.0101                           |
| 0.746                         | 0.0433                      | 0.60  | 0.846 | 0.0100                           |
| 0.656                         | 0.0492                      | 0.62  | 0.939 | 0.0102                           |
| 0.597                         | 0.0514                      | 0.91  | 0.970 | 0.0102                           |
| 0.528                         | 0.0528                      | 0.94  | 0.980 | 0.0102                           |
| 0.432                         | 0.0550                      | 0.96  | 0.990 | 0.0100                           |
| 0.394                         | 0.0568                      | 0.97  | 0.993 | 0.0100                           |
| 0.342                         | 0.0613                      | 0.98  | 0.998 | 0.0101                           |
| 0.306                         | 0.0647                      | 0.99  | 0.999 | 0.0101                           |
| 0.263                         | 0.0678                      | 1.00  | 1.000 | 0.0098                           |
| 0.224                         | 0.0751                      |       |       | 0.0097                           |
| 0.154                         | 0.112                       |       |       | 0.0107                           |
| 0.116                         | 0.162                       |       |       | 0.0096                           |
| 0.0879                        | 0.248                       |       |       | 0.0099                           |
| 0.0783                        | 0.296                       |       |       | 0.0097                           |
| 0.0721                        | 0.350                       |       |       | 0.0096                           |
| 0.0688                        | 0.443                       |       |       | 0.0099                           |
| 0.0683                        | 0.493                       |       |       | 0.0101                           |
| 0.0670                        | 0.540                       |       |       | 0.0101                           |
| 0.0613                        | 0.588                       |       |       | 0.0093                           |
| 0.0618                        | 0.686                       |       |       | 0.0095                           |
| 0.0628                        | 0.760                       |       |       | 0.0097                           |
| 0.0647                        | 0.839                       |       |       | 0.0099                           |
| 0.0639                        | 0.972                       |       |       | 0.0097                           |

Table VI. Experimental data  $\underline{C}_{\text{Ag}}$ ,  $\underline{C}_{\text{IO}_3}$  and  $\Delta \underline{E}$  from emf measurements.  $\Delta \underline{E}$  is the emf at the iodate concentration considered minus the emf at  $\underline{C}_{\text{IO}_3}=0$ . Calculated  $\underline{C}_{\text{Ag}}/[\text{Ag}^+]$  and  $[\text{IO}_3^-]$  are included for all investigated melts (Ag,K,Na) ( $\text{NO}_3, \text{IO}_3$ ).

$$\underline{T} = 524 \text{ K} ; \quad \underline{C}_{\text{Ag}} = 2.98 \times 10^{-3} \text{ mol kg}^{-1}$$

| $\underline{C}_{\text{IO}_3} / \text{mol kg}^{-1}$ | $\Delta \underline{E} / \text{mV}$ | $\underline{C}_{\text{Ag}} / [\text{Ag}^+]$ | $[\text{IO}_3^-] / \text{mol kg}^{-1}$ |
|----------------------------------------------------|------------------------------------|---------------------------------------------|----------------------------------------|
| 0.0096                                             | 0.6                                | 1.013                                       | 0.0095                                 |
| 0.0485                                             | 4.9                                | 1.115                                       | 0.0482                                 |
| 0.0876                                             | 9.4                                | 1.232                                       | 0.0870                                 |
| 0.1270                                             | 13.8                               | 1.358                                       | 0.1261                                 |
| 0.1658                                             | 18.0                               | 1.490                                       | 0.1646                                 |
| 0.2048                                             | 22.1                               | 1.632                                       | 0.2034                                 |
| 0.2830                                             | 29.9                               | 1.940                                       | 0.2811                                 |

$$\underline{T} = 524 \text{ K} ; \quad \underline{C}_{\text{Ag}} = 3.21 \times 10^{-3} \text{ mol kg}^{-1}$$

| $\underline{C}_{\text{IO}_3} / \text{mol kg}^{-1}$ | $\Delta \underline{E} / \text{mV}$ | $\underline{C}_{\text{Ag}} / [\text{Ag}^+]$ | $[\text{IO}_3^-] / \text{mol kg}^{-1}$ |
|----------------------------------------------------|------------------------------------|---------------------------------------------|----------------------------------------|
| 0.0096                                             | 0.5                                | 1.011                                       | 0.0095                                 |
| 0.0483                                             | 4.7                                | 1.110                                       | 0.0479                                 |
| 0.0872                                             | 8.8                                | 1.215                                       | 0.0865                                 |
| 0.1263                                             | 13.0                               | 1.334                                       | 0.1253                                 |
| 0.1651                                             | 17.2                               | 1.464                                       | 0.1639                                 |
| 0.2038                                             | 21.4                               | 1.607                                       | 0.2023                                 |
| 0.2426                                             | 25.4                               | 1.756                                       | 0.2408                                 |
| 0.2814                                             | 29.1                               | 1.906                                       | 0.2794                                 |

Table VI, continued.

$$\underline{T} = 538 \text{ K} ; \quad \underline{C}_{\text{Ag}} = 3.15 \times 10^{-3} \text{ mol kg}^{-1}$$

| $\underline{C}_{\text{IO}_3^-} / \text{mol kg}^{-1}$ | $\Delta \underline{E} / \text{mV}$ | $\underline{C}_{\text{Ag}} / [\text{Ag}^+]$ | $[\text{IO}_3^-] / \text{mol kg}^{-1}$ |
|------------------------------------------------------|------------------------------------|---------------------------------------------|----------------------------------------|
| 0.0098                                               | 0.6                                | 1.013                                       | 0.0097                                 |
| 0.0486                                               | 3.8                                | 1.085                                       | 0.0483                                 |
| 0.0875                                               | 7.9                                | 1.186                                       | 0.0869                                 |
| 0.1264                                               | 12.4                               | 1.307                                       | 0.1256                                 |
| 0.1653                                               | 17.1                               | 1.446                                       | 0.1642                                 |
| 0.2041                                               | 21.0                               | 1.573                                       | 0.2028                                 |
| 0.2430                                               | 24.5                               | 1.696                                       | 0.2415                                 |
| 0.2818                                               | 26.7                               | 1.779                                       | 0.2801                                 |

$$\underline{T} = 538 \text{ K} ; \quad \underline{C}_{\text{Ag}} = 3.4 \times 10^{-3} \text{ mol kg}^{-1}$$

| $\underline{C}_{\text{IO}_3^-} / \text{mol kg}^{-1}$ | $\Delta \underline{E} / \text{mV}$ | $\underline{C}_{\text{Ag}} / [\text{Ag}^+]$ | $[\text{IO}_3^-] / \text{mol kg}^{-1}$ |
|------------------------------------------------------|------------------------------------|---------------------------------------------|----------------------------------------|
| 0.0098                                               | 0.1                                | 1.002                                       | 0.0097                                 |
| 0.0489                                               | 4.1                                | 1.092                                       | 0.0485                                 |
| 0.0880                                               | 7.8                                | 1.184                                       | 0.0874                                 |
| 0.1266                                               | 11.6                               | 1.284                                       | 0.1257                                 |
| 0.1654                                               | 15.4                               | 1.394                                       | 0.1642                                 |
| 0.2432                                               | 23.0                               | 1.642                                       | 0.2416                                 |
| 0.2817                                               | 26.0                               | 1.752                                       | 0.2799                                 |

Table VI, continued.

$$\underline{T} = 538 \text{ K} ; \quad \underline{C}_{\text{Ag}} = 1.06 \times 10^{-3} \text{ mol kg}^{-1}$$

| $\underline{C}_{\text{IO}_3^-} / \text{mol kg}^{-1}$ | $\Delta \underline{E} / \text{mV}$ | $\underline{C}_{\text{Ag}} / [\text{Ag}^+]$ | $[\text{IO}_3^-] / \text{mol kg}^{-1}$ |
|------------------------------------------------------|------------------------------------|---------------------------------------------|----------------------------------------|
| 0.0099                                               | 1.0                                | 1.022                                       | 0.0099                                 |
| 0.0488                                               | 4.8                                | 1.109                                       | 0.0487                                 |
| 0.0877                                               | 8.6                                | 1.204                                       | 0.0875                                 |
| 0.1265                                               | 12.2                               | 1.301                                       | 0.1262                                 |
| 0.1654                                               | 16.0                               | 1.412                                       | 0.1650                                 |
| 0.2043                                               | 20.0                               | 1.539                                       | 0.2039                                 |
| 0.2434                                               | 23.6                               | 1.664                                       | 0.2429                                 |
| 0.2823                                               | 27.2                               | 1.798                                       | 0.2817                                 |

$$\underline{T} = 553 \text{ K} ; \quad \underline{C}_{\text{Ag}} = 3.02 \times 10^{-3} \text{ mol kg}^{-1}$$

| $\underline{C}_{\text{IO}_3^-} / \text{mol kg}^{-1}$ | $\Delta \underline{E} / \text{mV}$ | $\underline{C}_{\text{Ag}} / [\text{Ag}^+]$ | $[\text{IO}_3^-] / \text{mol kg}^{-1}$ |
|------------------------------------------------------|------------------------------------|---------------------------------------------|----------------------------------------|
| 0.0097                                               | 0.9                                | 1.019                                       | 0.0096                                 |
| 0.0486                                               | 5.3                                | 1.118                                       | 0.0483                                 |
| 0.0877                                               | 9.2                                | 1.213                                       | 0.0871                                 |
| 0.1269                                               | 13.5                               | 1.327                                       | 0.1261                                 |
| 0.1658                                               | 17.7                               | 1.449                                       | 0.1647                                 |
| 0.2045                                               | 21.5                               | 1.570                                       | 0.2032                                 |
| 0.2433                                               | 25.4                               | 1.703                                       | 0.2418                                 |
| 0.2820                                               | 29.0                               | 1.837                                       | 0.2803                                 |

Table VI, continued.

$$\underline{T} = 553 \text{ K} ; \quad \underline{C}_{\text{Ag}} = 3.09 \times 10^{-3} \text{ mol kg}^{-1}$$

| $\underline{C}_{\text{IO}_3} / \text{mol kg}^{-1}$ | $\Delta \underline{E} / \text{mV}$ | $\underline{C}_{\text{Ag}} / [\text{Ag}^+]$ | $[\text{IO}_3^-] / \text{mol kg}^{-1}$ |
|----------------------------------------------------|------------------------------------|---------------------------------------------|----------------------------------------|
| 0.0095                                             | 1.5                                | 1.032                                       | 0.0094                                 |
| 0.0481                                             | 4.5                                | 1.099                                       | 0.0478                                 |
| 0.0869                                             | 8.0                                | 1.183                                       | 0.0863                                 |
| 0.1257                                             | 12.2                               | 1.292                                       | 0.1249                                 |
| 0.1645                                             | 16.2                               | 1.405                                       | 0.1634                                 |
| 0.2030                                             | 20.0                               | 1.521                                       | 0.2017                                 |
| 0.2415                                             | 23.8                               | 1.647                                       | 0.2400                                 |
| 0.2801                                             | 27.4                               | 1.777                                       | 0.2784                                 |

$$\underline{T} = 553 \text{ K} ; \quad \underline{C}_{\text{Ag}} = 3.06 \times 10^{-2} \text{ mol kg}^{-1}$$

| $\underline{C}_{\text{IO}_3} / \text{mol kg}^{-1}$ | $\Delta \underline{E} / \text{mV}$ | $\underline{C}_{\text{Ag}} / [\text{Ag}^+]$ | $[\text{IO}_3^-] / \text{mol kg}^{-1}$ |
|----------------------------------------------------|------------------------------------|---------------------------------------------|----------------------------------------|
| 0.0486                                             | 4.9                                | 1.109                                       | 0.0455                                 |
| 0.0878                                             | 8.9                                | 1.206                                       | 0.0822                                 |
| 0.1264                                             | 12.7                               | 1.307                                       | 0.1185                                 |
| 0.1654                                             | 16.5                               | 1.416                                       | 0.1552                                 |
| 0.2045                                             | 20.3                               | 1.534                                       | 0.1922                                 |
| 0.2435                                             | 23.7                               | 1.648                                       | 0.2291                                 |
| 0.2823                                             | 27.3                               | 1.778                                       | 0.2660                                 |

Table VI, continued.

$$\underline{T} = 553 \text{ K}; \underline{C}_{\text{Ag}} = 3.08 \times 10^{-2} \text{ mol kg}^{-1}$$

| $\underline{C}_{\text{IO}_3}/\text{mol kg}^{-1}$ | $\underline{\Delta E}/\text{mV}$ | $\underline{C}_{\text{Ag}}/[\text{Ag}^+]$ | $[\text{IO}_3^-]/\text{mol kg}^{-1}$ |
|--------------------------------------------------|----------------------------------|-------------------------------------------|--------------------------------------|
| 0.0098                                           | 0.7                              | 1.015                                     | 0.0092                               |
| 0.0489                                           | 4.9                              | 1.109                                     | 0.0457                               |
| 0.0877                                           | 8.9                              | 1.206                                     | 0.0821                               |
| 0.1263                                           | 12.7                             | 1.307                                     | 0.1183                               |
| 0.1650                                           | 16.4                             | 1.413                                     | 0.1548                               |
| 0.2038                                           | 20.1                             | 1.528                                     | 0.1914                               |
| 0.2426                                           | 23.6                             | 1.645                                     | 0.2282                               |
| 0.2815                                           | 27.2                             | 1.774                                     | 0.2651                               |

$$\underline{T} = 553 \text{ K}; \underline{C}_{\text{Ag}} = 3.20 \times 10^{-3} \text{ mol kg}^{-1}$$

| $\underline{C}_{\text{IO}_3}/\text{mol kg}^{-1}$ | $\underline{\Delta E}/\text{mV}$ | $\underline{C}_{\text{Ag}}/[\text{Ag}^+]$ | $[\text{IO}_3^-]/\text{mol kg}^{-1}$ |
|--------------------------------------------------|----------------------------------|-------------------------------------------|--------------------------------------|
| 0.0094                                           | 1.0                              | 1.021                                     | 0.0093                               |
| 0.0485                                           | 5.2                              | 1.115                                     | 0.0482                               |
| 0.0873                                           | 10.7                             | 1.252                                     | 0.0867                               |
| 0.1263                                           | 15.0                             | 1.370                                     | 0.1254                               |
| 0.1649                                           | 19.1                             | 1.493                                     | 0.1638                               |
| 0.2037                                           | 23.0                             | 1.621                                     | 0.2024                               |
| 0.2425                                           | 26.6                             | 1.748                                     | 0.2409                               |
| 0.2816                                           | 30.0                             | 1.877                                     | 0.2798                               |

Table VI, continued.

$$\underline{T} = 553 \text{ K}; \underline{C}_{\text{Ag}} = 3.05 \times 10^{-3} \text{ mol kg}^{-1}$$

| $\underline{C}_{\text{IO}_3}/\text{mol kg}^{-1}$ | $\underline{\Delta E}/\text{mV}$ | $\underline{C}_{\text{Ag}}/[\text{Ag}^+]$ | $[\text{IO}_3^-]/\text{mol kg}^{-1}$ |
|--------------------------------------------------|----------------------------------|-------------------------------------------|--------------------------------------|
| 0.0094                                           | 0.9                              | 1.019                                     | 0.0093                               |
| 0.0480                                           | 4.6                              | 1.101                                     | 0.0477                               |
| 0.0862                                           | 8.6                              | 1.198                                     | 0.0856                               |
| 0.1248                                           | 12.3                             | 1.294                                     | 0.1240                               |
| 0.1634                                           | 16.6                             | 1.417                                     | 0.1623                               |
| 0.2021                                           | 20.4                             | 1.534                                     | 0.2008                               |
| 0.2406                                           | 23.8                             | 1.647                                     | 0.2391                               |
| 0.2792                                           | 27.5                             | 1.780                                     | 0.2775                               |

$$\underline{T} = 588 \text{ K}; \underline{C}_{\text{Ag}} = 2.96 \times 10^{-3} \text{ mol kg}^{-1}$$

| $\underline{C}_{\text{IO}_3}/\text{mol kg}^{-1}$ | $\underline{\Delta E}/\text{mV}$ | $\underline{C}_{\text{Ag}}/[\text{Ag}^+]$ | $[\text{IO}_3^-]/\text{mol kg}^{-1}$ |
|--------------------------------------------------|----------------------------------|-------------------------------------------|--------------------------------------|
| 0.0097                                           | 0.7                              | 1.014                                     | 0.0096                               |
| 0.0484                                           | 5.0                              | 1.104                                     | 0.0481                               |
| 0.0875                                           | 9.5                              | 1.206                                     | 0.0870                               |
| 0.1264                                           | 13.4                             | 1.303                                     | 0.1256                               |
| 0.1657                                           | 17.3                             | 1.407                                     | 0.1647                               |
| 0.2047                                           | 20.9                             | 1.511                                     | 0.2036                               |
| 0.2437                                           | 24.7                             | 1.629                                     | 0.2424                               |
| 0.2824                                           | 28.5                             | 1.756                                     | 0.2809                               |

Table VI, continued.

$$\underline{T} = 588 \text{ K}; \underline{C}_{\text{Ag}} = 3.05 \times 10^{-3} \text{ mol kg}^{-1}$$

| $\underline{C}_{\text{IO}_3} / \text{mol kg}^{-1}$ | $\Delta \underline{E} / \text{mV}$ | $\underline{C}_{\text{Ag}} / [\text{Ag}^+]$ | $[\text{IO}_3^-] / \text{mol kg}^{-1}$ |
|----------------------------------------------------|------------------------------------|---------------------------------------------|----------------------------------------|
| 0.0097                                             | 1.1                                | 1.022                                       | 0.0096                                 |
| 0.0489                                             | 6.1                                | 1.128                                       | 0.0486                                 |
| 0.0879                                             | 10.5                               | 1.230                                       | 0.0873                                 |
| 0.1269                                             | 14.6                               | 1.334                                       | 0.1261                                 |
| 0.1656                                             | 18.2                               | 1.433                                       | 0.1646                                 |
| 0.2045                                             | 22.0                               | 1.544                                       | 0.2033                                 |
| 0.2435                                             | 25.7                               | 1.661                                       | 0.2421                                 |
| 0.2826                                             | 29.3                               | 1.784                                       | 0.2811                                 |

$$\underline{T} = 622 \text{ K}; \underline{C}_{\text{Ag}} = 3.16 \times 10^{-3} \text{ mol kg}^{-1}$$

| $\underline{C}_{\text{IO}_3} / \text{mol kg}^{-1}$ | $\Delta \underline{E} / \text{mV}$ | $\underline{C}_{\text{Ag}} / [\text{Ag}^+]$ | $[\text{IO}_3^-] / \text{mol kg}^{-1}$ |
|----------------------------------------------------|------------------------------------|---------------------------------------------|----------------------------------------|
| 0.0097                                             | 1.1                                | 1.021                                       | 0.0096                                 |
| 0.0484                                             | 6.3                                | 1.125                                       | 0.0481                                 |
| 0.0872                                             | 10.4                               | 1.214                                       | 0.0867                                 |
| 0.1261                                             | 14.1                               | 1.301                                       | 0.1254                                 |
| 0.1650                                             | 17.2                               | 1.378                                       | 0.1641                                 |
| 0.2041                                             | 20.7                               | 1.472                                       | 0.2031                                 |
| 0.2432                                             | 24.4                               | 1.577                                       | 0.2420                                 |
| 0.2820                                             | 27.3                               | 1.668                                       | 0.2807                                 |

Table VI, continued.

$$\underline{T} = 622 \text{ K}; \underline{C}_{\text{Ag}} = 3.16 \times 10^{-3} \text{ mol kg}^{-1}$$

| $\underline{C}_{\text{IO}_3} / \text{mol kg}^{-1}$ | $\underline{\Delta E} / \text{mV}$ | $\underline{C}_{\text{Ag}} / [\text{Ag}^+]$ | $[\text{IO}_3^-] / \text{mol kg}^{-1}$ |
|----------------------------------------------------|------------------------------------|---------------------------------------------|----------------------------------------|
| 0.0094                                             | 1.1                                | 1.021                                       | 0.0093                                 |
| 0.0484                                             | 6.1                                | 1.121                                       | 0.0481                                 |
| 0.0872                                             | 10.5                               | 1.216                                       | 0.0867                                 |
| 0.1261                                             | 14.1                               | 1.301                                       | 0.1254                                 |
| 0.1649                                             | 17.5                               | 1.386                                       | 0.1640                                 |
| 0.2038                                             | 20.9                               | 1.477                                       | 0.2028                                 |
| 0.2426                                             | 24.2                               | 1.571                                       | 0.2414                                 |
| 0.2816                                             | 27.4                               | 1.667                                       | 0.2803                                 |

## Figure Captions

Figure 1.  $\underline{C}_{\text{Ag}}/[\text{Ag}^+] \text{ vs. } [\text{IO}_3^-]$  from three different emf titrations in 1:1 (K,Na)NO<sub>3</sub> at 553 K.  $\underline{C}_{\text{Ag}} = 3.02 \times 10^{-3} \text{ mol kg}^{-1}$  ( $\square$ ),  $3.06 \times 10^{-2} \text{ mol kg}^{-1}$  ( $\circ$ ), and  $3.08 \times 10^{-2} \text{ mol kg}^{-1}$  ( $\triangle$ ).

Figure 2. Mole fraction of NaIO<sub>3</sub> in the solid phase as a function of  $\underline{C}_{\text{IO}_3}$  in the melt. Filled symbols represent the Na-rich phase and half-filled symbols represent systems with a mixture of the two solid solutions (as indicated from X-ray diffraction at room temperature).

Figure 3. Activity of AgIO<sub>3</sub> as a function of  $\underline{x}_1$  in the solid phase. Filled symbols represent the Na-rich phase.

Figure 4. Solubility curve for AgIO<sub>3</sub> in 1:1 (K,Na)NO<sub>3</sub> at 553 K. Filled symbols represent melts in equilibrium with Na-rich solid solution after the phase transition.

Figure 5. The fraction  $\underline{\alpha}$  of Ag(I) present in different species in molten 1:1 (K,Na)NO<sub>3</sub> at 524 K and 588 K as a function of the iodate concentration in the limit  $\underline{C}_{\text{Ag}} \rightarrow 0$ . The graphs - calculated from the constants of Table II - represent from top to bottom  $\text{Ag}^+$ , AgIO<sub>3</sub> and  $\text{Ag}(\text{IO}_3)_2^-$ .

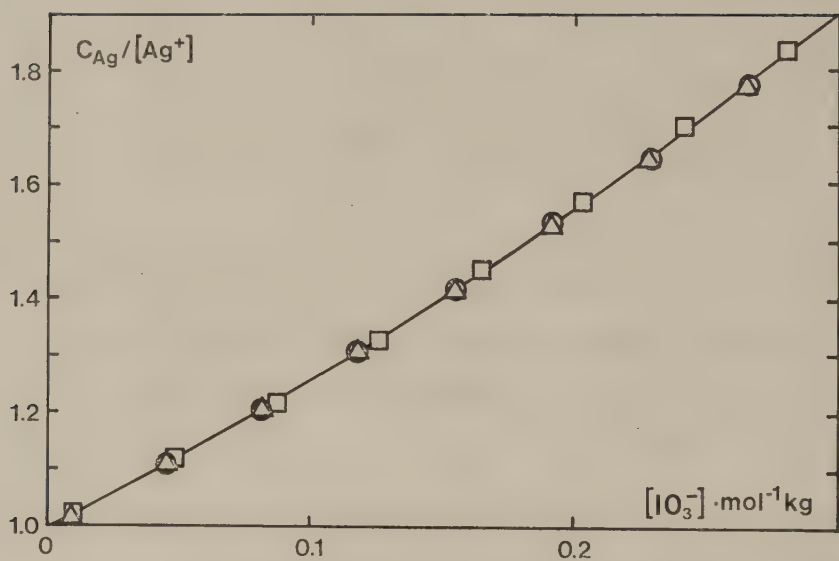


Figure 1.

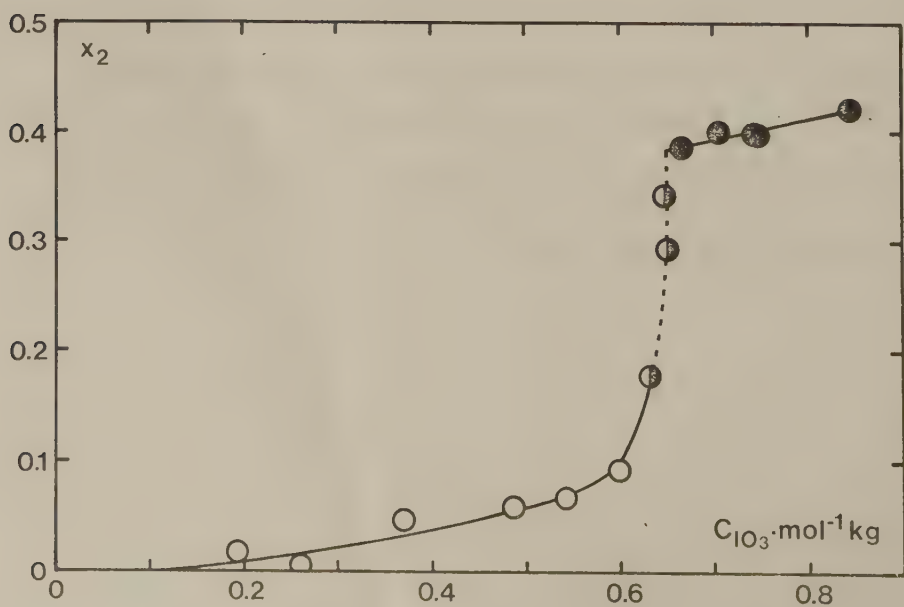


Figure 2.

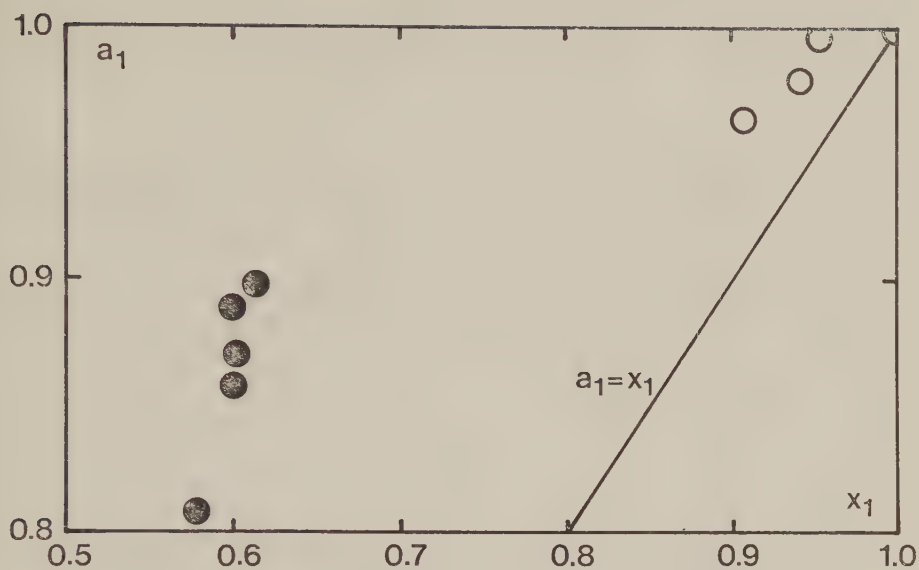


Figure 3.

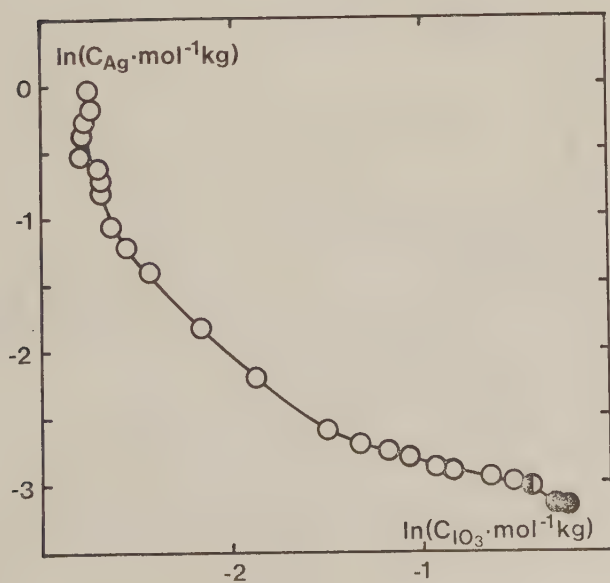


Figure 4.

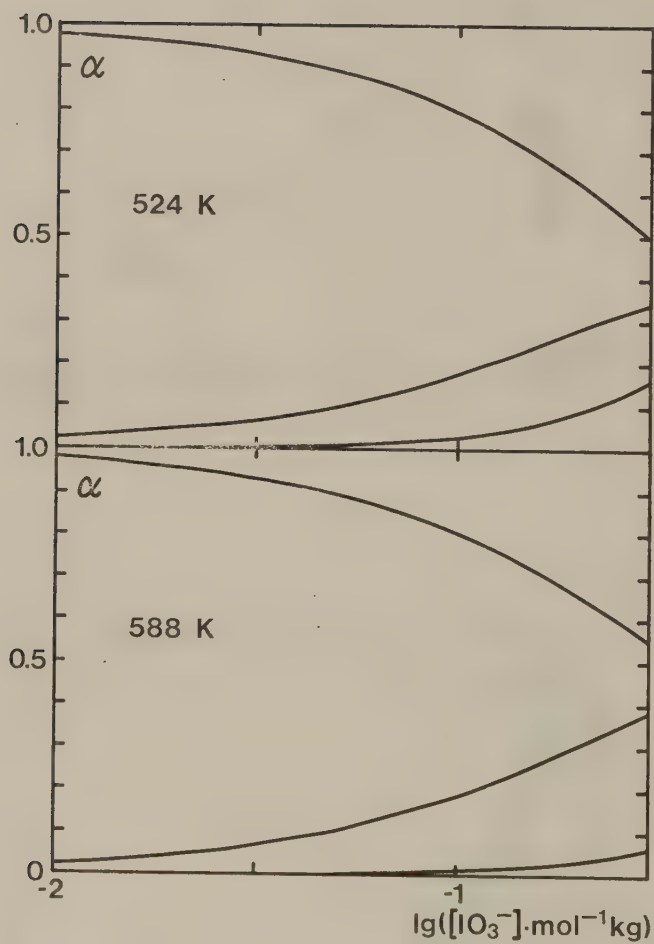


Figure 5.

Solid Solutions  $(\text{Ag,Na})_2\text{CrO}_4$  and Silver Chromate Complexes  
 in  $(\text{K,Na})\text{NO}_3$  Melts. A Potentiometric, Spectrophotometric  
 and Solubility Study.

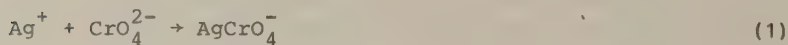
B. HOLMBERG\* and G. THOME

The complex formation between  $\text{Ag(I)}$  and  $\text{CrO}_4^{2-}$  in molten 1:1  $(\text{K,Na})\text{NO}_3$  has been studied mainly by emf and solubility measurements. Stability constants  $\beta$  for the rather weak complexes  $\text{AgCrO}_4^-$ ,  $\text{Ag}_2\text{CrO}_4$  and  $\text{Ag}(\text{CrO}_4)_2^{3-}$  have been determined. The emf measurements were performed at five temperatures between 523 K and 623 K. The temperature dependence of  $\beta_{11}$  is interpreted in terms of  $\Delta H_1^\circ$  and  $\Delta S_1^\circ$  for the formal process  $\text{Ag}^+ + \text{CrO}_4^{2-} \rightarrow \text{AgCrO}_4^-$ , which is favoured to about the same extent by  $\Delta H_1^\circ$  and  $-\Delta S_1^\circ$  contributions to  $\Delta G_1^\circ$  at 553 K. The solubility of a range of solid solutions  $(\text{Ag,Na})_2\text{CrO}_4$  has been measured at the reference temperature 553 K both in melts with  $\text{Ag}^+$  in excess over  $\text{CrO}_4^{2-}$  and vice versa. Stability constants obtained from these measurements agree with those from potentiometric data. The activity of  $\text{Ag}_2\text{CrO}_4$  in the solids has been determined. A phase transition from solid solutions of  $\text{Ag}_2\text{CrO}_4$  structure (I) to a Na-rich phase (II) with  $x_{\text{Na}} = 0.53 \pm 0.05$  was detected by thermodynamic methods and X-ray powder diffraction technique. Phase I is close to thermodynamically ideal whereas phase II exhibits large positive deviations from ideality. Absorption spectra of  $\text{CrO}_4^{2-}$  in melts with various cationic compositions show a remarkable shift of the low-energy band towards lower energies upon association with  $\text{Ag}^+$ . This is attributed to the occurrence of a considerable d- $\pi$ -back-donation from  $\text{Ag(I)}$  to  $\text{CrO}_4^{2-}$ .

## Introduction

In previous papers we have reported on the complexation of  $\text{NO}_2^-$ <sup>1</sup> and  $\text{IO}_3^-$ <sup>2</sup> with Ag(I) in the molten "standard solvent" equimolar (K,Na)NO<sub>3</sub>. Although the thermodynamic stability of complexes formed in those systems is comparably low, the silver ion may be considered as a good "probe" metal ion for comparing the complexing ability of various oxoanions, since the Ag(I) activity can be determined conveniently by emf measurements with silver electrodes. A number of emf studies of Ag(I) association with divalent oxoanions in various molten alkali nitrates have also appeared in the literature,<sup>3-7</sup> but the spread in the data - both with respect to temperature, solvent composition and complex stabilities - is unfortunately too large in most cases to make a meaningful comparison of e.g. enthalpy and entropy effects on the association in different systems possible. It is also in general desirable to use more than one experimental method to study the complexation in order to avoid misinterpretation of data.

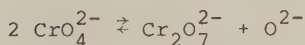
The complex formation between  $\text{CrO}_4^{2-}$  and Ag(I) has been studied in various molten alkali nitrates by Sacchetto and coworkers,<sup>6</sup> using emf measurements. The 1:1 complex  $\text{AgCrO}_4^-$  was considered only, but the data of what was said to be a preliminary set of measurements in equimolar (K,Na)NO<sub>3</sub> are too scattered to be used in a discussion of the thermodynamics of the association process, which can be schematically written as



In a similar study Alvarez-Funes and Hill determined the stability of  $\text{AgCrO}_4^-$  in molten  $\text{KNO}_3$ .<sup>7</sup>

In the present paper a more thorough investigation of the association and solubility equilibria in the system  $\text{Ag}, (\text{K}, \text{Na}) - \text{CrO}_4, \text{NO}_3$  is presented. The aim of the study is to examine which associated silver chromate species that exist in  $(\text{K}, \text{Na})\text{NO}_3$  melts - with special emphasis on the thermodynamics of process (1) - and to elucidate the heterogeneous equilibria between solid chromate phases and melts, since solid solution formation with  $\text{Ag}(\text{I})$  compounds has turned out to be of great importance in other systems.<sup>2,8</sup> The main information on these topics is obtained from potentiometry and solubility measurements, but a number of visible absorption spectra of  $\text{CrO}_4^{2-}$  in different cationic environments have also been recorded at 553 K. The spectral results will be considered in the discussion section of this paper.

The condensation of  $\text{CrO}_4^{2-}$  to  $\text{Cr}_2\text{O}_7^{2-}$  in molten equimolar  $(\text{K}, \text{Na})\text{NO}_3$  has been investigated by Kust.<sup>9</sup> The equilibrium constant for the reaction



is really very low,  $1.4 \times 10^{-8}$  at 553 K, but acid  $\text{Ag}^+$  ions might be expected to shift the equilibrium to the right. No indication of such an interfering reaction has been found by us, however, in the present study.

## Experimental section

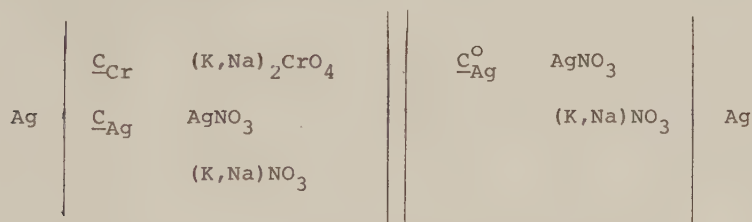
Silver nitrate, sodium nitrate and potassium nitrate (Merck p.a.) were pretreated and stored as described previously.<sup>10</sup> Alkali metal chromate was added as an equimolar mixture of sodium chromate (Baker analyzed reagent) and potassium chromate (Merck p.a.). These salts were dried separately, ground together and then dried again at 120 °C for several days prior to use. Silver chromate (Merck p.a.) was used without any further purification. In some cases, silver chromate was precipitated directly in the melt from added alkali chromate and silver nitrate.

Furnaces, temperature control and measurement and the construction of the cell for emf measurements have been described elsewhere.<sup>1,10,11</sup>

Solubility Measurements. Systems with approximately 3 g of  $\text{Ag}_2\text{CrO}_4$ , 75 g of  $(\text{K},\text{Na})\text{NO}_3$  and varying amounts of  $\text{AgNO}_3$  or  $(\text{K},\text{Na})_2\text{CrO}_4$  were agitated at 553 K for at least 50 h in Pyrex glass tubes. Some systems contained amounts of  $\text{Ag}_2\text{CrO}_4$  varying between 0.3 g and 10 g. Maximum concentrations were  $0.25 \text{ mol kg}^{-1}$   $(\text{K},\text{Na})_2\text{CrO}_4$  and  $0.5 \text{ mol kg}^{-1}$   $\text{AgNO}_3$ . (The solubility of alkali chromate in 1:1  $(\text{K},\text{Na})\text{NO}_3$  at 553 K was determined to be  $0.26 \pm 0.01 \text{ mol kg}^{-1}$ .) Samples from the nitrate phase were analysed for silver and chromate. Silver was determined by electroanalytical precipitation of Ag on a rotating platinum cathode from hot aqueous cyanide solutions after elimination of chromate by precipitation as  $\text{BaCrO}_4$ .

The total chromate concentration,  $\underline{C}_{Cr}$ , was determined spectrophotometrically in samples dissolved in water from the  $CrO_4^{2-}$  absorption at 370 nm for systems with  $\underline{C}_{Cr} > 2 \cdot 10^{-4}$  mol kg<sup>-1</sup> in the melt. At lower concentrations the more sensitive method employing diphenyl carbazide was used.<sup>12</sup> In the latter case silver had to be removed from the aqueous solution by precipitation with bromide before the addition of diphenyl carbazide. For systems containing more than 2 g of  $Ag_2CrO_4$  the equilibrium composition of the solid phase was calculated from the difference between added and found amounts of various ions in the nitrate melt.

Potentiometric Measurements. The following cell was used:



$\underline{C}_{Ag}$  and  $\underline{C}_{Ag}^O$  denote total concentrations of Ag(I) in test and reference melts, respectively. The cell was usually set up with 250 g of  $(K,Na)NO_3$  and 0.0025 mol kg<sup>-1</sup>  $AgNO_3$  in both cell compartments and left with vigorous stirring for about 18 hours. Successive additions of  $(K,Na)_2CrO_4$  were then made, and the emf,  $\underline{E}$ , was measured repeatedly at constant temperature over four different electrode combinations after each addition by means of a Digiscan 10 PRC datalogging unit from Mess + System Technik, München. The  $\underline{E}$ -values were measured to  $\pm 0.05$  mV. Stable readings were as a rule obtained within 30 min. after each addition of

chromate. In order to decide whether or not polynuclear species are present in melts with an excess of  $\text{CrO}_4^{2-}$  over  $\text{Ag}^+$  some series were run with  $\underline{C}_{\text{Ag}} = 0.0065 \text{ mol kg}^{-1}$  at  $280^\circ\text{C}$  as well. Eight different melt compositions were as a rule studied in each series; the maximum concentration of chromate was  $0.16 \text{ mol kg}^{-1}$ . All series of measurements were duplicated at least once. Data were recorded at five different temperatures in the range  $250 - 350^\circ\text{C}$ .

Absorption Spectra. The equipment used has been described elsewhere.<sup>13</sup> The spectra were recorded at  $553 \text{ K}$  in  $10 \text{ mm}$  fused silica cells with pure  $(\text{K},\text{Na})\text{NO}_3$  solvent as reference. The densities of the composite melts were determined by interpolation under the assumption that partial molar volumes of the constituents are independent of composition. Data from previous publications on  $\text{NaNO}_3$ ,  $\text{KNO}_3$  and binaries  $\text{NaNO}_3 - \text{AgNO}_3$  and  $\text{KNO}_3 - \text{AgNO}_3$  were used.<sup>14-16</sup> The possible errors introduced by this procedure are probably much smaller than the estimated uncertainty ( $\sim 5\%$ ) in the measured absorbances.

## Results from Potentiometric Measurements

Stability constants, defined by

$$\beta_{mn} = \frac{[Ag_m(CrO_4)^{\frac{m-n}{n}}]}{[Ag^+]^m [CrO_4^{2-}]^n} \quad (2)$$

are determined. Since junction potentials are negligible in these dilute ionic melts

$$\Delta E = \frac{RT}{F} \ln (C_{Ag} / [Ag^+]) \quad (3)$$

where  $\Delta E$  is  $E$  at the chromate concentration considered minus  $E$  at  $C_{Cr} = 0$  in the left hand compartment of the cell. Combination of eqns. (2) and (3) with the stoichiometric requirement

$$C_{Ag} = [Ag^+] + \sum_m \sum_n m [Ag_m(CrO_4)^{\frac{m-2n}{n}}] \quad (4)$$

yields

$$\exp\left(\frac{F}{R} \frac{\Delta E}{T}\right) = 1 + \sum_m \sum_n m \beta_{mn} [Ag^+]^{m-1} [CrO_4^{2-}]^n \quad (5)$$

It appeared that the left hand member of eqn. (5) could be accurately described by a second degree polynomial in  $[CrO_4^{2-}]$  independent of the  $Ag(I)$  content of the melts. Hence the complexes  $AgCrO_4^-$  and  $Ag(CrO_4)_2^{3-}$  are the only species that have to be considered in melts having chromate in excess over silver. This is exemplified by Fig. 1, displaying results from two series of measurements at 280 °C.

The final treatment of data was made by use of a computer program yielding the best fitting parameters  $\beta_{mn}$  from eqn. (5)

by minimizing the sum of squared errors  $(\Delta E_{\text{obs}} - \Delta E_{\text{calc}})^2$ . Table I gives stability constants from the emf measurements at five temperatures.

The thermodynamic parameters  $\Delta H_1^{\circ}$  and  $\Delta S_1^{\circ}$  for process (1) have been estimated from a study of  $\Delta G_1^{\circ} = -RT \ln \beta_{11}$  as a function of temperature. The standard state chosen relates to ionic fractions of unity.  $\Delta G_1^{\circ}$  is a good linear function of  $T$  so  $\Delta H_1^{\circ}$  and  $\Delta S_1^{\circ}$  have been estimated by linear regression with a weight scheme analogous to the one described in a previous paper.<sup>1</sup> The resulting parameters are  $\Delta H_1^{\circ} = (-6.0 \pm 1.6) \text{ kJ mol}^{-1}$  and  $\Delta S_1^{\circ} = (20 \pm 3) \text{ J K}^{-1} \text{ mol}^{-1}$ . Stated errors are one estimated standard deviation.

Data for the second step of complexation are not accurate enough to make a similar estimate of  $\Delta H_2^{\circ}$  and  $\Delta S_2^{\circ}$  possible.

### Results from Solubility Measurements

The solid phase. When the composition of the solid phases was determined after equilibration, it appeared that they contained stoichiometrically an excess of chromate relative to silver in most cases. In order to find out whether the counter ions to this excess chromate were  $\text{Na}^+$ ,  $\text{K}^+$  or both, systems with pure  $\text{KNO}_3$  and pure  $\text{NaNO}_3$  as solvents were prepared. Silver chromate (0.012 mol) was equilibrated with

$\text{KNO}_3$  (0.88 mol) or  $\text{NaNO}_3$  (0.88 mol) at  $350^\circ\text{C}$ . Analyses showed that the mole fraction of  $\text{Ag}_2\text{CrO}_4$ ,  $\underline{x}_1$ , in the solid phase was 0.92 in the sodium system, whereas no indication of any dissolution of  $\text{K}_2\text{CrO}_4$  into the  $\text{Ag}_2\text{CrO}_4$  phase could be detected in the potassium system. These findings gave the conclusion that sodium chromate from the  $(\text{K},\text{Na})\text{NO}_3$  based melts is dissolved into the solid silver chromate.

Fig. 2 gives the composition of the solid as a function of  $\underline{C}_{\text{Cr}}$  in the nitrate melt. The mole fraction  $\underline{x}_2$  of  $\text{Na}_2\text{CrO}_4$  in the  $(\text{Ag},\text{Na})_2\text{CrO}_4$  solid rises as  $\underline{C}_{\text{Cr}}$  increases, and around  $\underline{C}_{\text{Cr}} = 0.118 \text{ mol kg}^{-1}$  there is a steep increase in  $\underline{x}_2$  up to  $\underline{x}_2 = 0.53 \pm 0.05$ , which suggests a phase transition from what can be described as an  $\text{Ag}_2\text{CrO}_4$  based solid solution I to a Na-rich solid phase II with the lower composition limit  $\underline{x}_2 = 0.53$ . As this value is determined by extrapolation it is given with rather wide limits of error. As can be seen from Fig. 2 there is again a smooth increase in  $\underline{x}_2$  for phase II as  $\underline{C}_{\text{Cr}}$  is increased.

X-ray powder diffraction studies were made at room temperature on solids with  $\underline{x}_2 = 0.17$ , 0.49 and 0.85, as well as on pure  $\text{Ag}_2\text{CrO}_4$  and  $\text{Na}_2\text{CrO}_4$ . The diffraction pattern for phase I with  $\underline{x}_2 = 0.17$  was very similar to that of pure  $\text{Ag}_2\text{CrO}_4$  and could be indexed on the basis of the same symmetry as  $\text{Ag}_2\text{CrO}_4$  with very slight changes in the edge lengths. For phase II with  $\underline{x}_2 = 0.85$  the diffraction pattern was significantly different from those of  $\text{Ag}_2\text{CrO}_4$  and  $\text{Na}_2\text{CrO}_4$  which are both orthorhombic.<sup>17,18</sup> It could, however, be properly indexed on the basis of a monoclinic symmetry

with the cell parameters  $\underline{a} = 14.583(2) \text{ \AA}$ ,  $\underline{b} = 5.024(1) \text{ \AA}$ ,  $\underline{c} = 7.406(1) \text{ \AA}$  and  $\underline{\beta} = 97.19(3) \text{ deg.}$ .

For the powder with the formal composition  $\underline{x}_2 = 0.49$  we could observe significant diffraction lines from both phase I and II, which confirms the previous assumption that the transition I  $\rightarrow$  II takes place when the total equilibrium concentration  $\underline{C}_{\text{Cr}}$  is  $0.118 \text{ mol kg}^{-1}$ .

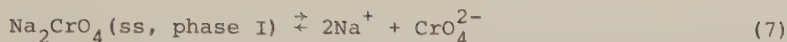
The activity  $\underline{a}_1$  of  $\text{Ag}_2\text{CrO}_4$  in the solid phase has to be known in order that solubility data may be used for the determination of complex ion stabilities.  $\underline{a}_1$  is computed from

$$\underline{a}_{1j} = \exp \left[ \frac{\ln R_j}{\ln R_0} (x_2/x_1) d \ln R \right] \quad (6)$$

where  $\underline{R} = (\underline{Y}^2 \cdot [\text{CrO}_4^{2-}])^{-1}$  and  $\underline{Y} = [\text{Na}^+]/([\text{Na}^+] + [\text{K}^+] + [\text{Ag}^+])^{8,19}$

The index  $j$  is used to denote different quantities referring to the same actual system and  $\underline{R}_0$  refers to a system with  $\underline{x}_1 = 1$  and  $\underline{a}_1 = 1$ , i.e. the standard state chosen for  $\text{Ag}_2\text{CrO}_4$ . Hence, the activity of  $\text{Ag}_2\text{CrO}_4$  in phase II also relates to pure  $\text{Ag}_2\text{CrO}_4$ . Fig. 3 gives  $\underline{a}_1$  as a function of  $\underline{x}_1$  in the two solid phases.

In phase I  $\underline{a}_1$  is well described by the ideal Temkin relation  $\underline{a}_1 = \underline{x}_1^2$  for  $0.8 \leq \underline{x}_1 \leq 1$ , and the solid solutions can thus be regarded as random mixtures of  $\text{Ag}^+$  and  $\text{Na}^+$  on cation positions in the  $\text{Ag}_2\text{CrO}_4$  lattice in this composition range. This implies that the activity of  $\text{Na}_2\text{CrO}_4$ ,  $\underline{a}_2$ , in phase I is given fairly well by  $\underline{a}_2 = \underline{x}_2^2$ . For the heterogeneous reaction



with the species of the right hand member present in the nitrate melt, an equilibrium constant  $K_{\text{Na}}^{\text{I}}$  may be defined as

$$K_{\text{Na}}^{\text{I}} = [\text{CrO}_4^{2-}] \gamma_{\text{Na}}^2 a_2^{-1} \quad (8)$$

The solubility data for the range  $0.016 \leq C_{\text{Cr}} \text{ mol}^{-1} \text{ kg} \leq 0.094$  (corresponding to  $0.07 \leq x_2 \leq 0.17$ ) have thus been utilized together with a set of  $[\text{CrO}_4^{2-}]$  from the stability constants calculation (next section) and the relation  $a_2 = x_2^2$  to yield a value of  $K_{\text{Na}}^{\text{I}} = (0.83 \pm 0.08) \text{ mol kg}^{-1}$ .

The  $a_1$  data obtained for phase II exhibit substantial deviations from ideal and normal regular solution behaviour (cf. Fig. 3). Fig. 3 shows that  $a_1$  tends to a constant value around 0.25 if  $x_1$  for phase II is extrapolated into the range  $0 \leq x_1 \leq 0.1$ . Since  $x_1 = 0$  demands  $a_1 = 0$ , this behaviour suggests that at least one more solid phase transition has to take place in that composition range. This prediction is also supported by the fact that the X-ray powder diffraction patterns of phase II ( $x_1 = 0.15$ ) and  $\text{Na}_2\text{CrO}_4$  are quite different.

Complexation in the range  $\frac{2C}{C_{\text{Cr}}} > \frac{C}{C_{\text{Ag}}}$ . Fig. 4 surveys the experimental material.

A general expression for the solubility "product" of  $\text{Ag}_2\text{CrO}_4$  is

$$\underline{K}_S = [\text{Ag}^+]^2 [\text{CrO}_4^{2-}] / \underline{a}_1 \quad (9)$$

By combination of eqn. (9) with eqns. (2) and (4) we obtain:

$$\underline{C}_{\text{Ag}} [\text{CrO}_4^{2-}]^{\frac{1}{2}} \underline{a}_1^{-\frac{1}{2}} = \underline{K}_S (1 + \sum_{\underline{m}} \sum_{\underline{n}} \underline{\beta}_{\underline{m} \underline{n}} [\text{Ag}^+]^{\underline{m}-1} [\text{CrO}_4^{2-}]^{\underline{n}}) \quad (10)$$

Inspection of the solubility curve shows that no species with more negative charge than - 3 are formed. Since emf measurements clearly show the absence of polynuclear complexes in this composition range, all data were treated according to eqn. (10), assuming  $\text{AgCrO}_4^-$  and  $\text{Ag}(\text{CrO}_4)_2^{3-}$  only. A second-degree polynomial in  $\text{CrO}_4^{2-}$  that describes the experimental data  $\underline{C}_{\text{Ag}} [\text{CrO}_4^{2-}]^{\frac{1}{2}} \underline{a}_1^{-\frac{1}{2}}$  can easily be found by iteration.  $\underline{K}_S^{\frac{1}{2}}$ ,  $\underline{K}_S^{\frac{1}{2}} \underline{\beta}_{11}$  and  $\underline{K}_S^{\frac{1}{2}} \underline{\beta}_{12}$  at 553 K are thus determined by a least-squares fit.  $\underline{K}_S$  and the stability constants are collected in Table II.

Complexation in the range  $\underline{C}_{\text{Ag}} > 2\underline{C}_{\text{Cr}}$ . In analogy with eqn. (10) we have

$$\underline{C}_{\text{Cr}} [\text{Ag}^+]^2 \underline{a}_1^{-1} = \underline{K}_S (1 + \sum_{\underline{m}} \sum_{\underline{n}} \underline{\beta}_{\underline{m} \underline{n}} [\text{Ag}^+]^{\underline{m}} [\text{CrO}_4^{2-}]^{\underline{n}-1}) \quad (11)$$

From the shape of the solubility curve it is clear that a neutral complex has to be taken into account in a proper description model. Any complex of the composition  $\text{Ag}_{2\underline{n}}(\text{CrO}_4)_{\underline{n}}$  may be considered, but we have made the reasonable assumption that the simplest species with the formal composition  $\text{Ag}_2\text{CrO}_4$  is formed.

It should be mentioned that for even higher values of  $\underline{C}_{Ag}$  than those displayed in Fig. 4 the solubility,  $\underline{C}_{Cr}$ , tends to increase with increasing  $\underline{C}_{Ag}$ . This might be taken as an indication of the presence of complexes with  $(\underline{m} - 2\underline{n}) > 0$ , but we have refrained from any quantitative treatment of data for these melts which are extremely concentrated in  $AgNO_3$ .

For the range covered by Fig. 4 the experimental data  $\underline{C}_{Cr} [Ag^+]^2 \underline{a}_1^{-1}$  are well described by a second degree polynomial in  $[Ag^+]$ . An iterative least squares calculation process yields  $\underline{K}_s$ ,  $\underline{K}_{s-11}$  and  $\underline{K}_{s-21}$  at 553 K. The results are found in Table II.

## Discussion

As might be expected the tendency of  $Ag^+$  to associate with  $CrO_4^{2-}$  is rather weak in molten alkali nitrate. Fig. 5 shows the relative amounts  $\underline{\alpha}$  of the different silvercontaining species as a function of  $[CrO_4^{2-}]$  in melts having  $CrO_4^{2-}$  in excess over  $Ag(I)$  at 524 K and at 622 K.  $Ag^+$  and  $AgCrO_4^-$  are the dominating species, and  $Ag(CrO_4)_2^{3-}$  contributes at most to only 9 % of  $\underline{C}_{Ag}$  at the lower temperature, 524 K, and is practically negligible at 622 K in the concentration range covered by our measurements. Fig. 6 gives an analogous overview of the stepwise attachment of  $Ag^+$  to one  $CrO_4^{2-}$  ion at

553 K. As can be seen from the distribution curves, the second complex  $\text{Ag}_2\text{CrO}_4$  is present in amounts quite comparable to those of  $\text{AgCrO}_4^-$  in melts of high  $\text{Ag}^+$  contents. The maximum fraction  $[\text{AgCrO}_4^-]/\underline{C}_{\text{Cr}}$  amounts to about 0.4 in such melts.

Table II displays a comparison between stability constants and  $\underline{K}_s$  determined by different methods at 553 K. Although the results agree within the estimated limits of uncertainty, it is quite evident that potentiometric data yield the most precise estimate of  $\beta_{11}$ . The large uncertainty in  $\beta_{12}$  from solubility data is an obvious consequence of the low stability of  $\text{Ag}(\text{CrO}_4)_2^{3-}$  in combination with the complications brought about by the  $\text{Na}^+ - \text{Ag}^+$  liquid - solid ion exchange in systems with melts of high  $\text{CrO}_4^{2-}$  contents. Due to the selective solubility of  $\text{Na}_2\text{CrO}_4$  in the solid phase the K:Na ratio of the melts was at most shifted from 1:1 to 1.18:1. The difference in cationic composition might influence the complexation to a slight extent, but such a systematic effect is obviously hidden within the wide limits of random errors.

Our value of  $\underline{K}_s = 6.4 \times 10^{-6} \text{ mol}^3 \text{ kg}^{-3}$ , which is obtained from both branches ( $\underline{C}_{\text{Ag}} > 2\underline{C}_{\text{Cr}}$  and  $2\underline{C}_{\text{Cr}} > \underline{C}_{\text{Ag}}$ ) of the solubility isotherm, compares badly with previous determinations. Brookes and Flengas<sup>20</sup> obtained  $\underline{K}_s = 1.3 \times 10^{-7} \text{ mol}^3 \text{ kg}^{-3}$  in 1:1 (K,Na) $\text{NO}_3$  at 553 K spectrophotometrically, and Flengas and Rideal<sup>21</sup> roughly estimated  $\underline{K}_s$  to be  $1.0 \times 10^{-6} \text{ mol}^3 \text{ kg}^{-3}$  in the same solvent at 523 K from emf titration data. These discrepancies are most probably due to the fact that the formation of solid solutions  $(\text{Ag,Na})_2\text{CrO}_4$  was disregarded in Refs.

Visual observations of chromate containing melts showed that the yellow  $\text{CrO}_4^{2-}$  colour tended to get more pale if  $\text{Ag}^+$  were present in high concentrations. A number of absorption spectra of chromate in different cation environments was therefore recorded at 553 K. Our primary aim was to see if any support for the interpretation of thermodynamic data in terms of complex formation with  $\text{Ag}^+$  could be found in the spectra. Fig. 7 compares three instructive absorption spectra. Spectrum 1 is due to absorption ( $\underline{A}_1$ ) by pure  $(\text{K,Na})_2\text{CrO}_4$  in  $(\text{K,Na})\text{NO}_3$  ( $\underline{C}_{\text{Cr}} = 1.2 \times 10^{-4} \text{ mol kg}^{-1}$  or  $2.3 \times 10^{-4} \text{ M}$ ). Spectrum 2 gives the absorbance  $\underline{A}_2$  from a melt with the same chromate concentration,  $1.2 \times 10^{-4} \text{ mol kg}^{-1}$ , and a large excess of  $\text{Ag}^+$  added as  $\text{AgNO}_3$  ( $\underline{C}_{\text{Ag}} = 0.20 \text{ mol kg}^{-1}$  or  $0.39 \text{ M}$ ). For the sake of comparison the absorbance  $\underline{A}_3$  of a chromate-free  $\text{AgNO}_3$  solution,  $0.20 \text{ mol kg}^{-1}$ , is also displayed in Fig. 7.

The low-energy band of charge-transfer character of  $\text{CrO}_4^{2-}$  in an alkali metal ion environment is found at the wavelength  $\lambda_{\text{max}} = 371 \text{ nm}$  with a molar absorption coefficient  $\epsilon_{\text{max}} = 3.30 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$  in good agreement with the observations by Brookes and Flengas.<sup>20</sup> Spectrum 3 shows that the presence of  $\text{AgNO}_3$  in the alkali nitrate melt causes a relatively strong absorption in the 355 nm region, close to the UV absorption edge of the  $(\text{K,Na})\text{NO}_3$  solvent itself. (Changes in refractive index are estimated to affect the absorbance to less than 1 %.) This absorption peak also appears in spectrum 2 of course, but since  $\underline{C}_{\text{Ag}}$  is the same in melts 2 and 3 and since  $\underline{C}_{\text{Cr}} \ll \underline{C}_{\text{Ag}}$  in melt 2 the absorbance due to chromate

species only can be derived simply as  $\underline{A}_2 - \underline{A}_3$ . This is the dashed curve of Fig. 7.

$\underline{A}_1$  and the dashed curve  $\underline{A}_2 - \underline{A}_3$  are directly comparable, since  $\underline{C}_{Cr}$  is the same and the calculated mass densities only differ by an amount of 2 %. Previously published data show that changes in cation environments in ionic melts influence this absorption band, which has been ascribed to the  $t_1 \rightarrow e$  transition<sup>22</sup> in  $CrO_4^{2-}$ , to a very small extent. This is clear from the data collected in Table III. Smith and Boston<sup>24</sup> have also observed that the spectral profiles of this band in pure  $LiNO_3$  and  $CsNO_3$  closely follow that for  $KNO_3$ . The effect of the presence of  $Ag^+$  in the  $(K,Na)NO_3$  melt (less than 2 % of the total cation content) is thus remarkably large in view of these general observations. It can be seen from Fig. 6 that our solubility data predict a distribution of chromate in melt 2 as  $6 \times 10^{-5} \text{ mol kg}^{-1} CrO_4^{2-}$ ,  $4 \times 10^{-5} \text{ mol kg}^{-1} AgCrO_4^-$  and  $2 \times 10^{-5} \text{ mol kg}^{-1} Ag_2CrO_4$ . The absorbance contribution from only  $AgCrO_4^-$  and  $Ag_2CrO_4$  can therefore be deduced by subtraction of  $0.50 \underline{A}_1$  from  $\underline{A}_2 - \underline{A}_3$ . The result is represented by the dotted spectrum of Fig. 7: a broad field of absorption in the 360 - 440 nm region with an indication of two maxima around 385 nm and 400 nm.

The dotted spectrum could of course be tentatively regarded as consisting of two partially overlapping bands with individual maxima at about 380 nm and 400 nm due to  $AgCrO_4^-$  and  $Ag_2CrO_4$  respectively. At the present state such an assignment would be of a too speculative nature, but the matter certainly deserves a more quantitative and exhaustive experimental study than this preliminary one. Qualitatively, however, the shift

towards lower energies upon  $\text{Ag}^+$  association is rather interesting. A significant cation - oxygen  $\sigma$ -bonding, utilizing the oxygen lone-pair electrons, should rather be expected to change the absorption band towards higher energies. Such spectral changes have been observed upon e.g. protonation of  $\text{CrO}_4^{2-}$  to  $\text{HCrO}_4^-$  with  $\lambda_{\text{max}}$  shifted from 370 nm to 351 nm.<sup>27,28</sup> Therefore it seems probable that the change towards lower energies for the Ag-coordinated  $\text{CrO}_4^{2-}$  ion in nitrate melts is a result of an additional d- $\pi$ -back-donation of electrons from silver to chromate. The spectral observations discussed here thus furnish strong evidence for the existence of complexes with a chemical interaction between  $\text{Ag(I)}$  and  $\text{CrO}_4^{2-}$  which is fundamentally different from the alkali metal -  $\text{CrO}_4^{2-}$  interactions in the nitrate melts.

The quasi-lattice theory<sup>29</sup> has been used by Sacchetto and coworkers<sup>6</sup> in an attempt to rationalize data for  $\text{Ag(I)}$  association with  $\text{CrO}_4^{2-}$  in nitrate melts. Our results, however, clearly demonstrate the inapplicability of the quasi-lattice formalism for systems of this kind, containing polyvalent polyatomic ions. The apparent pair association energy  $\Delta A_1$  of the model tends to be strongly temperature dependent. A coordination number of 5 yields  $d\Delta A_1/dT = (-9 \pm 2) \text{ J mol}^{-1} \text{ K}^{-1}$ , which - for reasons discussed in a previous paper on iodate complexation<sup>2</sup> - is incompatible with both internal entropy and mixed solvent effects.<sup>6</sup>

Our analysis of the thermodynamics for the formation of  $\text{AgCrO}_4^-$ , schematically described by process (1), shows that the association reaction is favoured to approximately the same extent

by its exothermic character and by the gain in entropy at 553 K. This pattern is somewhat different from that of the  $\text{Ag}^+ - \text{IO}_3^-$  association in the same solvent, which is driven by a large entropy gain only.<sup>2</sup> The minute  $\Delta H_1^0$  for the  $\text{IO}_3^-$  association was found to be about the expected one if contributions from changes in electrostatic interactions between hard-sphere model ions were considered only. An analogous model calculation for the  $\text{CrO}_4^{2-}$  association should probably consider the uncomplexed  $\text{CrO}_4^{2-}$  as selectively  $\text{Na}^+$ -solvated. A hard-sphere interchange with  $\text{Ag}^+$  would then yield a positive contribution to  $\Delta H_1^0$ . The absolute magnitude of such an electrostatic contribution is very much depending on the choice of effective radius for  $\text{CrO}_4^{2-}$ , but one is inclined to believe that the covalent character of the  $\text{Ag}^+ - \text{CrO}_4^{2-}$  bonding - as evidenced by the spectral changes - most probably causes a larger energy gain than  $-6 \text{ kJ mol}^{-1}$ , which is the over-all enthalpy change.

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Supplementary Material Available. Tables IV and V, giving all experimental data from solubility and emf measurements (8 pages). Ordering information is given on any current masthead page.

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Table I. The over-all stability constants  $\beta_{11}$  and  $\beta_{12}$  for  $\text{Ag}^+ - \text{CrO}_4^{2-}$  complexes in molten 1:1 (K,Na) $\text{NO}_3$  from emf measurements. The limits of error are 95 % confidence limits.

| $T/K$ | $\beta_{11}/\text{mol}^{-1} \text{ kg}$ | $\beta_{12}/\text{mol}^{-2} \text{ kg}^2$ |
|-------|-----------------------------------------|-------------------------------------------|
| 524   | $4.0 \pm 0.2$                           | $7.9 \pm 1.8$                             |
| 538   | $3.9 \pm 0.1$                           | $6.0 \pm 0.7$                             |
| 553   | $4.1 \pm 0.1$                           | $3.6 \pm 1.1$                             |
| 588   | $3.5 \pm 0.2$                           | $5.0 \pm 1.3$                             |
| 622   | $3.30 \pm 0.05$                         | $2.3 \pm 0.7$                             |

Table II. Stability constants and  $K_s$  for  $\text{Ag}_2\text{CrO}_4$  in 1:1 (K,Na) $\text{NO}_3$  at 553 K determined by different experimental methods. The errors are 95 % confidence limits.

| $K_s \times 10^6 / \text{mol}^3 \text{ kg}^{-3}$ | $\beta_{11}/\text{mol}^{-1} \text{ kg}$ | $\beta_{12}/\text{mol}^{-2} \text{ kg}^2$ | $\beta_{21}/\text{mol}^{-2} \text{ kg}^2$ | Method                                |
|--------------------------------------------------|-----------------------------------------|-------------------------------------------|-------------------------------------------|---------------------------------------|
| $6.4 \pm 0.4$                                    | $3.6 \pm 1.2$                           | -                                         | $8 \pm 3$                                 | sol. $C_{\text{Ag}} > 2C_{\text{Cr}}$ |
| $6.4 \pm 1.0$                                    | $4.2 \pm 2.6$                           | $4 \pm 10$                                | -                                         | sol. $2C_{\text{Cr}} > C_{\text{Ag}}$ |
| -                                                | $4.1 \pm 0.1$                           | $3.6 \pm 1.1$                             | -                                         | emf                                   |

Table III. Characteristics of the low-energy absorption band of  $\text{CrO}_4^{2-}$  in aqueous solution and ionic melts.

| Medium                                   | $T/K$ | $\lambda_{\text{max}}/\text{nm}$ | $\epsilon_{\text{max}} \times 10^{-3}/\text{M}^{-1}\text{cm}^{-1}$ | Ref.      |
|------------------------------------------|-------|----------------------------------|--------------------------------------------------------------------|-----------|
| $\text{H}_2\text{O}$                     | 298   | 370                              | 4.10                                                               | 23        |
| $\text{KNO}_3$                           | 635   | 371                              | 3.38                                                               | 24        |
| $(\text{K},\text{Na})\text{NO}_3$ , 1:1  | 553   | 371                              | 3.60                                                               | 20        |
| $(\text{K},\text{Na})\text{NO}_3$ , 1:1  | 553   | 371                              | 3.30                                                               | This work |
| $(\text{K},\text{Li})\text{NO}_3$ , eut. | 433   | 369                              | 3.62                                                               | 25, 26    |
| $(\text{K},\text{Li})\text{Cl}$ , eut.   | 643   | 371                              | 3.08                                                               | 24        |

Table IV. Data on the solubility of  $(\text{Ag,Na})_2\text{CrO}_4$  in 1:1  $(\text{K,Na})\text{NO}_3$  melts at 553 K.  $\underline{K}_S$  is computed from  $[\text{Ag}^+]$  and  $[\text{CrO}_4^{2-}]$  (as computed from the appropriate stability constants of Table II) and the activities from column four.

| $\underline{C}_{\text{Cr}}/\text{mol kg}^{-1}$ | $\underline{C}_{\text{Ag}}/\text{mol kg}^{-1}$ | $\underline{x}_1$ | $\underline{a}_1$ | $\underline{K}_S \times 10^6/\text{mol}^3 \text{ kg}^{-3}$ |
|------------------------------------------------|------------------------------------------------|-------------------|-------------------|------------------------------------------------------------|
| 0.236                                          | $5.71 \cdot 10^{-3}$                           | 0.117             | 0.246             | 6.41                                                       |
| 0.228                                          | 5.72 "                                         | 0.149             | 0.246             | 6.49                                                       |
| 0.225                                          | 5.87 "                                         | 0.183             | 0.246             | 6.86                                                       |
| 0.217                                          | 6.08 "                                         | 0.233             | 0.266             | 6.87                                                       |
| 0.203                                          | 5.70 "                                         | 0.320             | 0.289             | 5.62                                                       |
| 0.149                                          | 7.19 "                                         | 0.431             | 0.484             | 5.40                                                       |
| 0.118                                          | 9.50 "                                         | 0.512             | -                 | 6.74                                                       |
| 0.111                                          | 9.64 "                                         | 0.734             | 0.674             | 6.61                                                       |
| 0.0935                                         | 0.0101                                         | 0.830             | 0.707             | 6.54                                                       |
| 0.0704                                         | 0.0112                                         | 0.852             | 0.749             | 6.68                                                       |
| 0.0617                                         | 0.0106                                         | 0.868             | 0.763             | 5.48                                                       |
| 0.0334                                         | 0.0136                                         | 0.900             | 0.829             | 5.47                                                       |
| 0.0165                                         | 0.0204                                         | 0.935             | 0.885             | 6.32                                                       |
| 0.0119                                         | 0.0237                                         | -                 | 0.920             | 6.27                                                       |
| 0.0116                                         | 0.0239                                         | -                 | 0.921             | 6.22                                                       |
| 0.0116                                         | 0.0243                                         | -                 | 0.922             | 6.41                                                       |
| $9.29 \cdot 10^{-3}$                           | 0.0277                                         | 0.959             | 0.933             | 6.61                                                       |
| 9.04 "                                         | 0.0281                                         | 0.955             | 0.934             | 6.62                                                       |
| 7.76 "                                         | 0.0284                                         | 0.958             | 0.938             | 5.82                                                       |
| 7.09 "                                         | 0.0321                                         | 0.961             | 0.943             | 6.70                                                       |
| 6.20 "                                         | 0.0349                                         | 0.964             | 0.949             | 6.86                                                       |
| 5.18 "                                         | 0.0355                                         | 0.969             | 0.955             | 5.92                                                       |
| 5.55 "                                         | 0.0361                                         | 0.968             | 0.953             | 6.54                                                       |
| 3.22 "                                         | 0.0500                                         | 0.977             | 0.971             | 6.93                                                       |
| 1.76 "                                         | 0.0645                                         | -                 | 0.983             | 5.99                                                       |
| 1.17 "                                         | 0.0831                                         | 0.991             | 0.993             | 6.17                                                       |
| $4.70 \cdot 10^{-4}$                           | 0.153                                          | 1.000             | 1.000             | 6.64                                                       |
| 1.95 "                                         | 0.278                                          |                   |                   | 6.15                                                       |
| 1.60 "                                         | 0.351                                          |                   |                   | 6.51                                                       |
| 1.28 "                                         | 0.431                                          |                   |                   | 6.34                                                       |

Table V. Experimental data  $\underline{C}_{Ag}$ ,  $\underline{C}_{Cr}$  and  $\Delta E$  from emf measurements.  $\Delta E$  is the emf at the chromate concentration considered minus the emf at  $\underline{C}_{Cr} = 0$ . Calculated  $\underline{C}_{Ag}/[Ag^+]$  and  $[CrO_4^{2-}]$  are included.

$$\underline{T} = 524 \text{ K} ; \underline{C}_{Ag} = 2.55 \times 10^{-3} \text{ mol kg}^{-1}$$

| $\underline{C}_{Cr}/\text{mol kg}^{-1}$ | $\Delta E/\text{mv}$ | $\underline{C}_{Ag}/[Ag^+]$ | $[CrO_4^{2-}]/\text{mol kg}^{-1}$ |
|-----------------------------------------|----------------------|-----------------------------|-----------------------------------|
| 0.0019                                  | 0.3                  | 1.007                       | 0.0019                            |
| 0.0247                                  | 4.2                  | 1.097                       | 0.0245                            |
| 0.0471                                  | 8.4                  | 1.204                       | 0.0466                            |
| 0.0695                                  | 12.1                 | 1.307                       | 0.0688                            |
| 0.0923                                  | 16.2                 | 1.431                       | 0.0914                            |
| 0.1150                                  | 19.8                 | 1.550                       | 0.1139                            |
| 0.1375                                  | 23.7                 | 1.690                       | 0.1362                            |
| 0.1596                                  | 27.1                 | 1.822                       | 0.1582                            |

$$\underline{T} = 524 \text{ K} ; \underline{C}_{Ag} = 2.79 \times 10^{-3} \text{ mol kg}^{-1}$$

| $\underline{C}_{Cr}/\text{mol kg}^{-1}$ | $\Delta E/\text{mV}$ | $\underline{C}_{Ag}/[Ag^+]$ | $[CrO_4^{2-}]/\text{mol kg}^{-1}$ |
|-----------------------------------------|----------------------|-----------------------------|-----------------------------------|
| 0.0111                                  | 2.0                  | 1.045                       | 0.0110                            |
| 0.0334                                  | 6.2                  | 1.147                       | 0.0330                            |
| 0.0558                                  | 10.3                 | 1.256                       | 0.0552                            |
| 0.0782                                  | 14.2                 | 1.370                       | 0.0774                            |
| 0.1007                                  | 18.2                 | 1.497                       | 0.0997                            |
| 0.1233                                  | 21.3                 | 1.603                       | 0.1220                            |
| 0.1457                                  | 25.1                 | 1.744                       | 0.1442                            |
| 0.1683                                  | 30.0                 | 1.944                       | 0.1667                            |

Table V, continued.

$$\underline{T} = 524 \text{ K} ; \underline{C}_{\text{Ag}} = 2.52 \times 10^{-3} \text{ mol kg}^{-1}$$

| $\underline{C}_{\text{Cr}}/\text{mol kg}^{-1}$ | $\Delta \underline{E}/\text{mV}$ | $\underline{C}_{\text{Ag}}/[\text{Ag}^+]$ | $[\text{CrO}_4^{2-}]/\text{mol kg}^{-1}$ |
|------------------------------------------------|----------------------------------|-------------------------------------------|------------------------------------------|
| 0.0111                                         | 2.1                              | 1.048                                     | 0.0110                                   |
| 0.0335                                         | 6.1                              | 1.145                                     | 0.0332                                   |
| 0.0559                                         | 9.7                              | 1.240                                     | 0.0554                                   |
| 0.0783                                         | 13.9                             | 1.361                                     | 0.0775                                   |
| 0.1008                                         | 17.4                             | 1.471                                     | 0.0999                                   |
| 0.1233                                         | 20.6                             | 1.579                                     | 0.1222                                   |
| 0.1458                                         | 24.6                             | 1.725                                     | 0.1445                                   |
| 0.1681                                         | 29.9                             | 1.940                                     | 0.1666                                   |

$$\underline{T} = 524 \text{ K} ; \underline{C}_{\text{Ag}} = 2.60 \times 10^{-3} \text{ mol kg}^{-1}$$

| $\underline{C}_{\text{Cr}}/\text{mol kg}^{-1}$ | $\Delta \underline{E}/\text{mV}$ | $\underline{C}_{\text{Ag}}/[\text{Ag}^+]$ | $[\text{CrO}_4^{2-}]/\text{mol kg}^{-1}$ |
|------------------------------------------------|----------------------------------|-------------------------------------------|------------------------------------------|
| 0.0020                                         | 0.3                              | 1.007                                     | 0.0020                                   |
| 0.0244                                         | 4.4                              | 1.102                                     | 0.0242                                   |
| 0.0472                                         | 8.4                              | 1.204                                     | 0.0467                                   |
| 0.0696                                         | 12.2                             | 1.310                                     | 0.0689                                   |
| 0.0921                                         | 15.9                             | 1.422                                     | 0.0912                                   |
| 0.1144                                         | 19.1                             | 1.530                                     | 0.1133                                   |
| 0.1368                                         | 22.3                             | 1.638                                     | 0.1355                                   |
| 0.1593                                         | 25.4                             | 1.755                                     | 0.1578                                   |

Table V, continued.

$$\underline{T} = 538 \text{ K} ; \underline{C}_{\text{Ag}} = 2.59 \times 10^{-3} \text{ mol kg}^{-1}$$

| $\underline{C}_{\text{Cr}}/\text{mol kg}^{-1}$ | $\Delta \underline{E}/\text{mV}$ | $\underline{C}_{\text{Ag}}/[\text{Ag}^+]$ | $[\text{CrO}_4^{2-}]/\text{mol kg}^{-1}$ |
|------------------------------------------------|----------------------------------|-------------------------------------------|------------------------------------------|
| 0.0020                                         | 0.2                              | 1.004                                     | 0.0020                                   |
| 0.0246                                         | 4.2                              | 1.095                                     | 0.0244                                   |
| 0.0471                                         | 8.2                              | 1.193                                     | 0.0466                                   |
| 0.0697                                         | 12.0                             | 1.295                                     | 0.0690                                   |
| 0.0919                                         | 15.8                             | 1.406                                     | 0.0911                                   |
| 0.1144                                         | 19.6                             | 1.526                                     | 0.1134                                   |
| 0.1368                                         | 23.0                             | 1.642                                     | 0.1356                                   |
| 0.1592                                         | 26.4                             | 1.767                                     | 0.1579                                   |

$$\underline{T} = 538 \text{ K} ; \underline{C}_{\text{Ag}} = 2.58 \times 10^{-3} \text{ mol kg}^{-1}$$

| $\underline{C}_{\text{Cr}}/\text{mol kg}^{-1}$ | $\Delta \underline{E}/\text{mV}$ | $\underline{C}_{\text{Ag}}/[\text{Ag}^+]$ | $[\text{CrO}_4^{2-}]/\text{mol kg}^{-1}$ |
|------------------------------------------------|----------------------------------|-------------------------------------------|------------------------------------------|
| 0.0019                                         | 0.4                              | 1.009                                     | 0.0019                                   |
| 0.0245                                         | 4.3                              | 1.097                                     | 0.0243                                   |
| 0.0470                                         | 8.4                              | 1.199                                     | 0.0466                                   |
| 0.0695                                         | 12.4                             | 1.306                                     | 0.0689                                   |
| 0.0920                                         | 16.2                             | 1.418                                     | 0.0912                                   |
| 0.1144                                         | 19.4                             | 1.519                                     | 0.1134                                   |
| 0.1369                                         | 23.1                             | 1.645                                     | 0.1357                                   |
| 0.1594                                         | 26.6                             | 1.774                                     | 0.1581                                   |

Table V, continued.

$\underline{T} = 553 \text{ K} ; \underline{C}_{\text{Ag}} = 2.72 \times 10^{-3} \text{ mol kg}^{-1}$

| $\underline{C}_{\text{Cr}}/\text{mol kg}^{-1}$ | $\Delta \underline{E}/\text{mV}$ | $\underline{C}_{\text{Ag}}/[\text{Ag}^+]$ | $[\text{CrO}_4^{2-}]/\text{mol kg}^{-1}$ |
|------------------------------------------------|----------------------------------|-------------------------------------------|------------------------------------------|
| 0.0019                                         | 0.2                              | 1.004                                     | 0.0019                                   |
| 0.0243                                         | 4.1                              | 1.090                                     | 0.0240                                   |
| 0.0469                                         | 8.2                              | 1.188                                     | 0.0464                                   |
| 0.0691                                         | 12.0                             | 1.286                                     | 0.0684                                   |
| 0.0919                                         | 15.8                             | 1.393                                     | 0.0911                                   |
| 0.1145                                         | 19.5                             | 1.505                                     | 0.1135                                   |
| 0.1369                                         | 22.9                             | 1.616                                     | 0.1357                                   |
| 0.1597                                         | 26.3                             | 1.736                                     | 0.1584                                   |

$\underline{T} = 553 \text{ K} ; \underline{C}_{\text{Ag}} = 2.57 \times 10^{-3} \text{ mol kg}^{-1}$

| $\underline{C}_{\text{Cr}}/\text{mol kg}^{-1}$ | $\Delta \underline{E}/\text{mV}$ | $\underline{C}_{\text{Ag}}/[\text{Ag}^+]$ | $[\text{CrO}_4^{2-}]/\text{mol kg}^{-1}$ |
|------------------------------------------------|----------------------------------|-------------------------------------------|------------------------------------------|
| 0.0020                                         | 0.2                              | 1.004                                     | 0.0020                                   |
| 0.0241                                         | 4.1                              | 1.090                                     | 0.0239                                   |
| 0.0463                                         | 8.0                              | 1.183                                     | 0.0458                                   |
| 0.0687                                         | 11.8                             | 1.281                                     | 0.0680                                   |
| 0.0909                                         | 16.0                             | 1.399                                     | 0.0901                                   |
| 0.1134                                         | 19.5                             | 1.505                                     | 0.1125                                   |
| 0.1358                                         | 22.7                             | 1.610                                     | 0.1347                                   |
| 0.1538                                         | 25.9                             | 1.721                                     | 0.1571                                   |

Table V, continued.

$$\underline{T} = 553 \text{ K} ; \underline{C}_{\text{Ag}} = 6.50 \times 10^{-3} \text{ mol kg}^{-1}$$

| $\underline{C}_{\text{Cr}}/\text{mol kg}^{-1}$ | $\Delta \underline{E}/\text{mV}$ | $\underline{C}_{\text{Ag}}/[\text{Ag}^+]$ | $[\text{CrO}_4^{2-}]/\text{mol kg}^{-1}$ |
|------------------------------------------------|----------------------------------|-------------------------------------------|------------------------------------------|
| 0.0021                                         | 0.3                              | 1.006                                     | 0.0020                                   |
| 0.0167                                         | 3.0                              | 1.065                                     | 0.0163                                   |
| 0.0313                                         | 5.8                              | 1.129                                     | 0.0306                                   |
| 0.0458                                         | 8.4                              | 1.193                                     | 0.0447                                   |
| 0.0603                                         | 11.0                             | 1.259                                     | 0.0589                                   |
| 0.0750                                         | 13.6                             | 1.330                                     | 0.0733                                   |
| 0.0896                                         | 16.4                             | 1.410                                     | 0.0876                                   |
| 0.1042                                         | 18.8                             | 1.483                                     | 0.1020                                   |

$$\underline{T} = 553 \text{ K} ; \underline{C}_{\text{Ag}} = 6.18 \times 10^{-3} \text{ mol kg}^{-1}$$

| $\underline{C}_{\text{Cr}}/\text{mol kg}^{-1}$ | $\Delta \underline{E}/\text{mV}$ | $\underline{C}_{\text{Ag}}/[\text{Ag}^+]$ | $[\text{CrO}_4^{2-}]/\text{mol kg}^{-1}$ |
|------------------------------------------------|----------------------------------|-------------------------------------------|------------------------------------------|
| 0.0020                                         | 0.4                              | 1.008                                     | 0.020                                    |
| 0.0164                                         | 3.0                              | 1.065                                     | 0.0160                                   |
| 0.0311                                         | 5.8                              | 1.129                                     | 0.0304                                   |
| 0.0457                                         | 8.3                              | 1.190                                     | 0.0447                                   |
| 0.0604                                         | 10.8                             | 1.254                                     | 0.0590                                   |
| 0.0748                                         | 13.4                             | 1.324                                     | 0.0732                                   |
| 0.0896                                         | 15.8                             | 1.393                                     | 0.0878                                   |
| 0.1043                                         | 18.4                             | 1.471                                     | 0.1022                                   |

Table V, continued.

 $\underline{T} = 588 \text{ K} ; \underline{C}_{\text{Ag}} = 2.40 \times 10^{-3} \text{ mol kg}^{-1}$ 

| $\underline{C}_{\text{Cr}}/\text{mol kg}^{-1}$ | $\Delta \underline{E}/\text{mV}$ | $\underline{C}_{\text{Ag}}/[\text{Ag}^+]$ | $[\text{CrO}_4^{2-}]/\text{mol kg}^{-1}$ |
|------------------------------------------------|----------------------------------|-------------------------------------------|------------------------------------------|
| 0.0020                                         | 0.4                              | 1.008                                     | 0.0020                                   |
| 0.0249                                         | 4.6                              | 1.095                                     | 0.0247                                   |
| 0.0471                                         | 8.6                              | 1.185                                     | 0.0467                                   |
| 0.0696                                         | 12.4                             | 1.277                                     | 0.0691                                   |
| 0.0919                                         | 16.2                             | 1.377                                     | 0.0912                                   |
| 0.1142                                         | 19.7                             | 1.475                                     | 0.1133                                   |
| 0.1367                                         | 23.0                             | 1.574                                     | 0.1357                                   |
| 0.1590                                         | 26.5                             | 1.687                                     | 0.1579                                   |

 $\underline{T} = 588 \text{ K} ; \underline{C}_{\text{Ag}} = 2.63 \times 10^{-3} \text{ mol kg}^{-1}$ 

| $\underline{C}_{\text{Cr}}/\text{mol kg}^{-1}$ | $\Delta \underline{E}/\text{mV}$ | $\underline{C}_{\text{Ag}}/[\text{Ag}^+]$ | $[\text{CrO}_4^{2-}]/\text{mol kg}^{-1}$ |
|------------------------------------------------|----------------------------------|-------------------------------------------|------------------------------------------|
| 0.0243                                         | 3.6                              | 1.074                                     | 0.0241                                   |
| 0.0469                                         | 7.5                              | 1.159                                     | 0.0465                                   |
| 0.0692                                         | 11.2                             | 1.247                                     | 0.0686                                   |
| 0.0915                                         | 15.1                             | 1.347                                     | 0.0907                                   |
| 0.1138                                         | 18.9                             | 1.452                                     | 0.1129                                   |
| 0.1363                                         | 22.2                             | 1.550                                     | 0.1352                                   |
| 0.1585                                         | 25.4                             | 1.651                                     | 0.1572                                   |

 $\underline{T} = 588 \text{ K} ; \underline{C}_{\text{Ag}} = 2.60 \times 10^{-3} \text{ mol kg}^{-1}$ 

| $\underline{C}_{\text{Cr}}/\text{mol kg}^{-1}$ | $\Delta \underline{E}/\text{mV}$ | $\underline{C}_{\text{Ag}}/[\text{Ag}^+]$ | $[\text{CrO}_4^{2-}]/\text{mol kg}^{-1}$ |
|------------------------------------------------|----------------------------------|-------------------------------------------|------------------------------------------|
| 0.0110                                         | 1.7                              | 1.034                                     | 0.0109                                   |
| 0.0333                                         | 5.7                              | 1.119                                     | 0.0330                                   |
| 0.0555                                         | 9.5                              | 1.206                                     | 0.0550                                   |
| 0.0778                                         | 13.1                             | 1.295                                     | 0.0771                                   |
| 0.1228                                         | 20.3                             | 1.493                                     | 0.1218                                   |
| 0.1674                                         | 27.3                             | 1.715                                     | 0.1661                                   |

Table V, continued.

$$\underline{T} = 622 \text{ K} ; \underline{C}_{\text{Ag}} = 2.50 \times 10^{-3} \text{ mol kg}^{-1}$$

| $\underline{C}_{\text{Cr}}/\text{mol kg}^{-1}$ | $\Delta \underline{E}/\text{mV}$ | $\underline{C}_{\text{Ag}}/[\text{Ag}^+]$ | $[\text{CrO}_4^{2-}]/\text{mol kg}^{-1}$ |
|------------------------------------------------|----------------------------------|-------------------------------------------|------------------------------------------|
| 0.0114                                         | 2.0                              | 1.038                                     | 0.0113                                   |
| 0.0338                                         | 5.8                              | 1.114                                     | 0.0335                                   |
| 0.0563                                         | 9.5                              | 1.194                                     | 0.0559                                   |
| 0.0787                                         | 13.1                             | 1.277                                     | 0.0781                                   |
| 0.1010                                         | 16.5                             | 1.361                                     | 0.1003                                   |
| 0.1235                                         | 19.9                             | 1.450                                     | 0.1227                                   |
| 0.1461                                         | 23.2                             | 1.542                                     | 0.1452                                   |
| 0.1683                                         | 26.2                             | 1.631                                     | 0.1672                                   |

$$\underline{T} = 622 \text{ K} ; \underline{C}_{\text{Ag}} = 2.75 \times 10^{-3} \text{ mol kg}^{-1}$$

| $\underline{C}_{\text{Cr}}/\text{mol kg}^{-1}$ | $\Delta \underline{E}/\text{mV}$ | $\underline{C}_{\text{Ag}}/[\text{Ag}^+]$ | $[\text{CrO}_4^{2-}]/\text{mol kg}^{-1}$ |
|------------------------------------------------|----------------------------------|-------------------------------------------|------------------------------------------|
| 0.0115                                         | 2.2                              | 1.042                                     | 0.0114                                   |
| 0.0340                                         | 5.8                              | 1.114                                     | 0.0337                                   |
| 0.0564                                         | 9.4                              | 1.192                                     | 0.0559                                   |
| 0.0789                                         | 12.8                             | 1.270                                     | 0.0783                                   |
| 0.1016                                         | 16.3                             | 1.355                                     | 0.1008                                   |
| 0.1244                                         | 19.8                             | 1.447                                     | 0.1235                                   |
| 0.1470                                         | 23.1                             | 1.538                                     | 0.1460                                   |
| 0.1699                                         | 26.2                             | 1.648                                     | 0.1687                                   |

## Figure Legends

Figure 1.  $\underline{C}_{\text{Ag}}/[\text{Ag}^+]$  vs.  $[\text{CrO}_4^{2-}]$  from two emf titrations in 1:1 (K,Na)NO<sub>3</sub> at 553 K.  $\underline{C}_{\text{Ag}} = 0.0065 \text{ mol kg}^{-1}$  (○) and  $\underline{C}_{\text{Ag}} = 0.0026 \text{ mol kg}^{-1}$  (□). The full-drawn curve is calculated from the stability constants of Table I.

Figure 2. The fraction  $\underline{x}_2$  of Na<sub>2</sub>CrO<sub>4</sub> in the solid phase as a function of  $\underline{C}_{\text{Cr}}$  in the melt.

Symbols: phase I (○); phase II (●).

The half-filled symbol represent a formal value for a probable mixture of I and II at the transition point.

Figure 3. The activity  $\underline{a}_1$  of Ag<sub>2</sub>CrO<sub>4</sub> as a function of  $\underline{x}_1$  in the solids.

Symbols: phase I (○); phase II (●). The curve represents  $\underline{a}_1 = \underline{x}_1^2$ .

Figure 4. Solubility curve for (Ag,Na)<sub>2</sub>CrO<sub>4</sub> in 1:1 (K,Na)NO<sub>3</sub> at 553 K. Open symbols represent melts in equilibrium with phase I, filled symbols with phase II.

Figure 5. The fraction  $\underline{\alpha}$  of Ag(I) present in different species in molten 1:1 (K,Na)NO<sub>3</sub> at 524 K and 622 K as a function of the chromate concentration in the limit  $\underline{C}_{\text{Ag}} \rightarrow 0$ . The graphs are calculated from the constants of Table I.

Figure 6. The fraction  $\underline{\alpha}$  of CrO<sub>4</sub><sup>2-</sup> present in different species in molten 1:1 (K,Na)NO<sub>3</sub> at 553 K as a function of  $[\text{Ag}^+]$  in the limit  $\underline{C}_{\text{Cr}} \rightarrow 0$ . The graphs are calculated by

use of the values  $\beta_{11} = 3.6 \text{ mol}^{-1} \text{ kg}$  and  $\beta_{21} = 8 \text{ mol}^{-2} \text{ kg}^2$  (cf. Table II).

Figure 7. The absorbance  $\underline{A}$  for solutions of  $\underline{1}:1.2 \times 10^{-4} \text{ mol kg}^{-1} (\text{K,Na})_2\text{CrO}_4 (\underline{A}_1)$ ,  $\underline{2}:1.2 \times 10^{-4} \text{ mol kg}^{-1} (\text{K,Na})_2\text{CrO}_4 + 0.20 \text{ mol kg}^{-1} \text{AgNO}_3 (\underline{A}_2)$  and  $\underline{3}:0.20 \text{ mol kg}^{-1} \text{AgNO}_3 (\underline{A}_3)$  in molten  $1:1 (\text{K,Na})\text{NO}_3$  at  $553 \text{ K}$  in  $10.00 \text{ mm}$  cell. The spectra are recorded vs. pure solvent. Difference curves:  $\underline{A}_2 - \underline{A}_3$  (dashed) and  $\underline{A}_2 - \underline{A}_3 - 0.50\underline{A}_1$  (dotted).

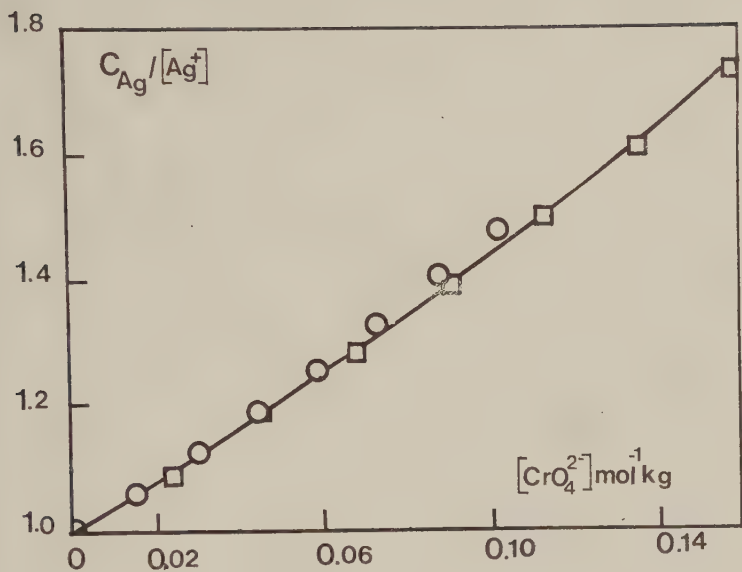


Figure 1.

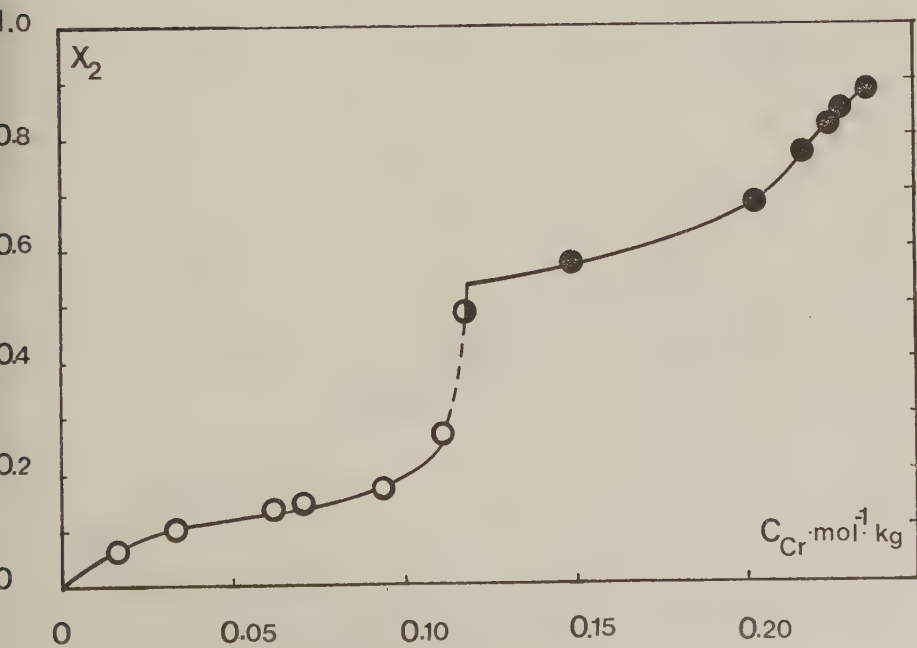


Figure 2.

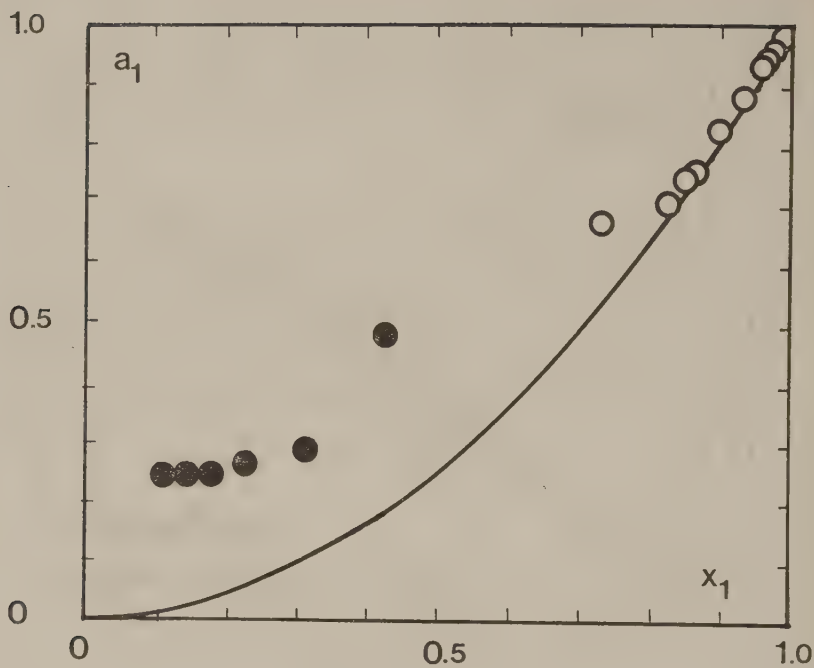


Figure 3.

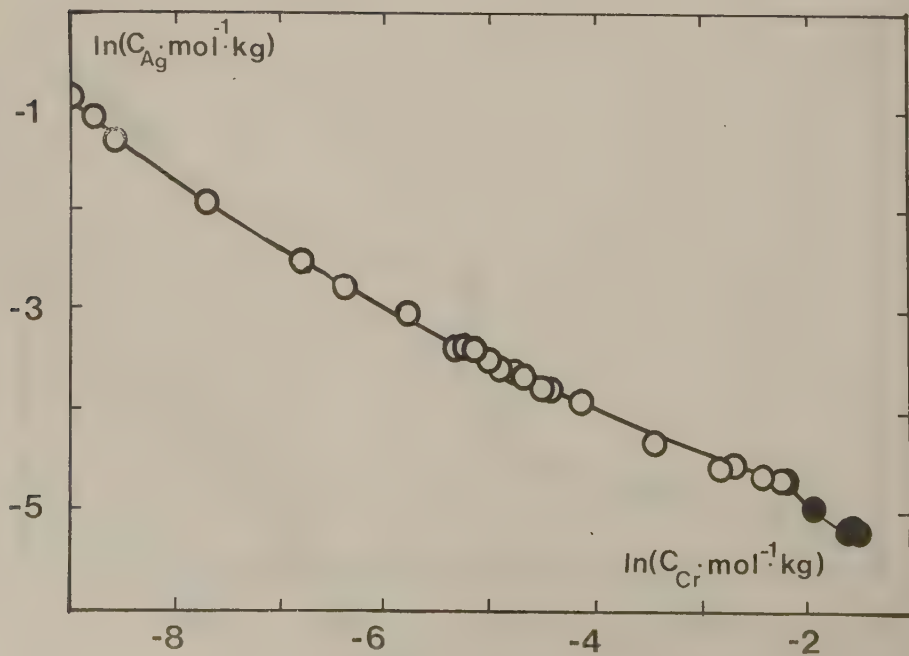


Figure 4.

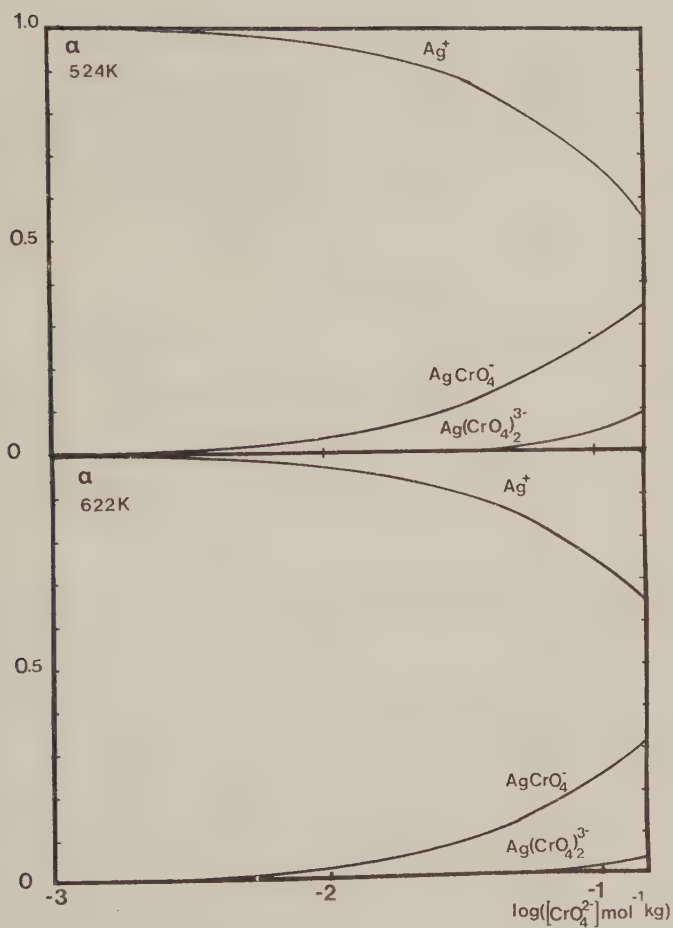


Figure 5.

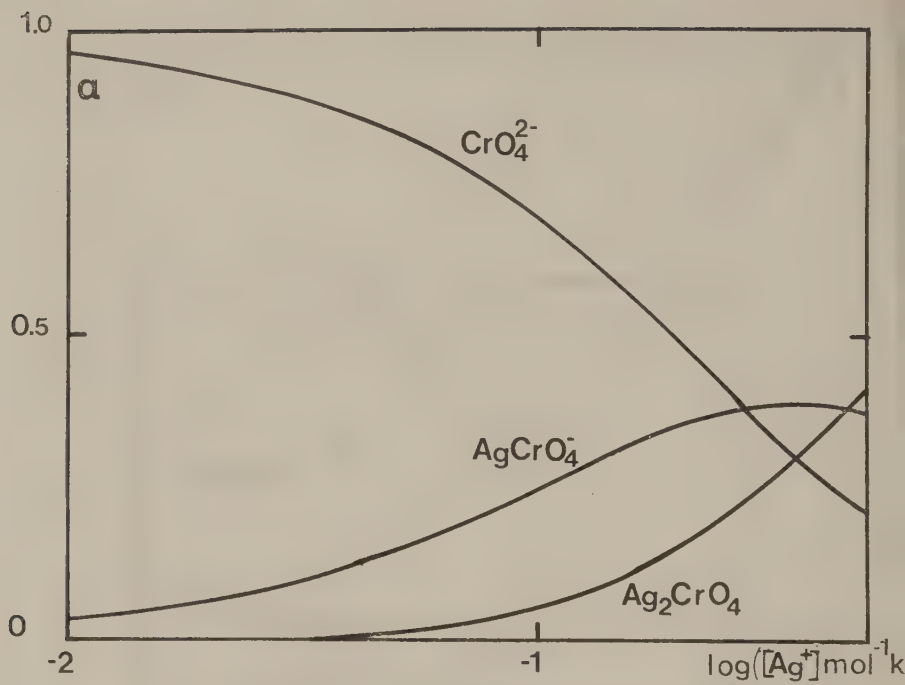


Figure 6.

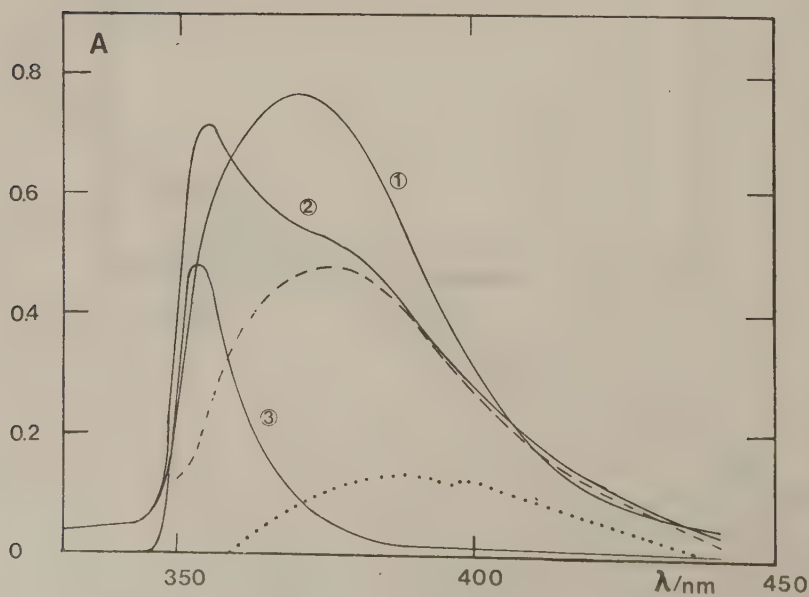


Figure 7.

Thermodynamics of Solid Solutions  $(\text{Ag,Na})_2\text{MoO}_4$  and  
Silver Molybdate Complexation in Molten  $(\text{K,Na})\text{NO}_3$ .  
A Potentiometric and Solubility Study.

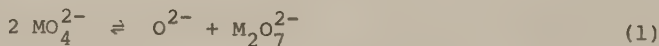
By Bertil Holmberg\* and Göran Thomé, Department of  
Physical Chemistry 1, Chemical Center, University  
of Lund, P.O. Box 740, S-220 07 Lund 7, Sweden

The complexes  $\text{AgMoO}_4^-$ ,  $\text{Ag}_2\text{MoO}_4$  and  $\text{Ag}(\text{MoO}_4)_2^{3-}$  have been shown to exist in molten 1:1  $(\text{K,Na})\text{NO}_3$  and the corresponding stability constants have been determined by potentiometry and solubility measurements. The complexes are weak, and emf measurements give by far the best estimate of  $\beta_{11}$  for  $\text{AgMoO}_4^-$ . Changes in  $\beta_{11}$  in the interval  $524 \text{ K} < T < 622 \text{ K}$  are analysed in terms of  $\Delta H_1^{\circ}$  and  $\Delta S_1^{\circ}$  for the association process.  $\Delta H_1^{\circ}$  and  $-T\Delta S_1^{\circ}$  contribute to about the same extent to  $\Delta G_1^{\circ}$ . This thermodynamic pattern is rather similar to that of  $\text{AgCrO}_4^-$  formation in the same solvent, but the present results indicate a possibility of a slightly stronger Ag - O bonding in the  $\text{MoO}_4^{2-}$  system. A continuous range of solid solutions  $(\text{Ag,Na})_2\text{MoO}_4$  with the Ag(I) fraction ranging from 1 to 0.4 has been observed at 553 K. An analysis of distribution equilibria between solids and melts show that the  $(\text{Ag,Na})_2\text{MoO}_4$  solids can be treated as regular cationic substitutional solutions with an interaction parameter  $\underline{A} = (9.6 \pm 0.5) \text{ kJ mol}^{-1}$ .

## Introduction

In a series of Ag(I) -oxoanion equilibria studies in molten 1:1 (K,Na)NO<sub>3</sub> we have recently described the nitrite<sup>1</sup> and the iodate<sup>2</sup> systems. These studies are now being extended to charge unsymmetrical systems containing divalent oxoligands, MO<sub>4</sub><sup>2-</sup> of the chromium group metals in an attempt to systematize the effects of charge, size etc of oxoanions on their complexing ability in an ionic oxoion solvent. The basic chemistry of these ions in molten alkali nitrates is fairly well known.

Kust<sup>3</sup> determined the equilibrium constants for the dimerization processes



for M = Cr, Mo and W in molten equimolar (K,Na)NO<sub>3</sub>. At 553 K these constants are  $1.2 \cdot 10^{-8}$ ,  $3.1 \cdot 10^{-8}$  and  $6.9 \cdot 10^{-4}$  for Cr, Mo and W respectively. This set of constants shows the much more basic character of the WO<sub>4</sub><sup>2-</sup> ion. For CrO<sub>4</sub><sup>2-</sup> and MoO<sub>4</sub><sup>2-</sup> negligible amounts of dimer are formed in the pure (K,Na)NO<sub>3</sub> solvent in the concentration range suitable for studies of complexation with cations.

Sacchetto and coworkers<sup>4</sup> have considered the formation of AgMoO<sub>4</sub><sup>-</sup> only in an attempt to apply the quasi-lattice formalism to charge unsymmetrical systems in nitrate melts. In a recent study of the Ag<sup>+</sup> - CrO<sub>4</sub><sup>2-</sup> system in (K,Na)NO<sub>3</sub> melts the inapplicability of this formalism to the AgCrO<sub>4</sub><sup>-</sup> formation process was, however, clearly demonstrated by us.<sup>5</sup> In addition to AgCrO<sub>4</sub><sup>-</sup> the species Ag<sub>2</sub>CrO<sub>4</sub> and Ag(CrO<sub>4</sub>)<sub>2</sub><sup>3-</sup> were also detected. The present work thus aims at a more complete picture of the Ag<sup>+</sup> - MoO<sub>4</sub><sup>2-</sup> association with special emphasis on the thermodynamics of the first step of complexation. The major part of information is obtained from potentiometric measurements in the range 524 K - 622 K. An additional solubility study has also been made at one reference temperature, chosen to be 553 K. The purpose of

the solubility measurements is of course to provide comparable information on the complexation from an independent method of study, but also to investigate the nature of the solid  $\text{Ag}_2\text{MoO}_4$  phase. Solid - liquid equilibration with ionic melts has turned out to be a powerful method of detecting solid solutions and of investigating the thermodynamics of such solutions.<sup>2,5,6</sup>

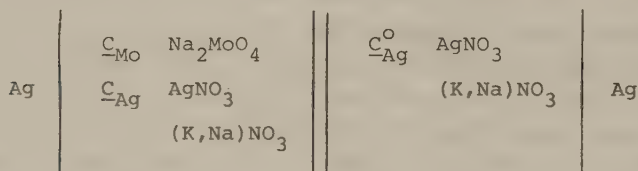
In the present case there are two conflicting statements about the  $\text{Ag}_2\text{MoO}_4$  -  $\text{Na}_2\text{MoO}_4$  subsystem in the literature. Belyaev and Doroshenko<sup>7</sup> claim that the components form a continuous range of solid solutions below 819 K whereas Sinistri and coworkers<sup>8</sup> state that the system is a simple eutectic one.

## Experimental

Chemicals. Silver nitrate, sodium nitrate and potassium nitrate (Merck p.a.) were pretreated and stored as described elsewhere.<sup>9</sup> Alkali molybdate was added to the melts as  $\text{Na}_2\text{MoO}_4$ . Reagent grade  $\text{Na}_2\text{MoO}_4 \cdot 2 \text{H}_2\text{O}$  (Merck) was ground and dried at 120°C for several days to constant weight, indicating the loss of two  $\text{H}_2\text{O}$  per formula unit.  $\text{Ag}_2\text{MoO}_4$  was prepared from aqueous solutions of  $\text{AgNO}_3$  and  $\text{Na}_2\text{MoO}_4$ , dried at 120°C for several days and stored in desiccator. The purity was checked by analysis for Ag. Result: theoretical Ag 57.4%, found 57.2%. X-ray powder diffraction analysis showed that the  $\beta$ -modification of  $\text{Ag}_2\text{MoO}_4$ <sup>11</sup> was obtained.

Equipment. Furnaces, measurement and control of temperature, emf measurement equipment and construction of the cell have been described previously.<sup>1,9,10</sup>

Emf Measurements. The following cell was used:



where  $\underline{C}_{\text{Mo}}$  and  $\underline{C}_{\text{Ag}}$  stand for total concentrations of molybdate and silver, respectively. The cell was usually set up with 250 g of  $(\text{K,Na})\text{NO}_3$  and  $\underline{C}_{\text{Ag}} = 0.001 \text{ mol kg}^{-1}$  and left with vigorous stirring for at least 18 hours before additions of sodium molybdate were made. The concentration of  $\text{AgNO}_3$  in the reference half-cell,  $\underline{C}_{\text{Ag}}^{\circ}$ , was  $0.001 \text{ mol kg}^{-1}$  in all series. The emf was measured repeatedly at constant temperature over four different electrode combinations after a number of successive additions of molybdate. Eight different compositions were as a rule studied in each series; the maximum concentration of molybdate was  $0.12 \text{ mol kg}^{-1}$ . The  $\underline{E}$ -values were measured to  $\pm 0.05 \text{ mV}$ . Stable readings were obtained within less than 30 min. All series of measurements were duplicated at least once. In order to decide whether or not polynuclear complexes (e.g.  $\text{Ag}_2\text{MoO}_4$ ) are to be considered in these melts with  $\underline{C}_{\text{Mo}} \gg \underline{C}_{\text{Ag}}$  some runs were also made with  $\underline{C}_{\text{Ag}} = 5 \times 10^{-4} \text{ mol kg}^{-1}$  and  $2 \times 10^{-4} \text{ mol kg}^{-1}$ . Data were recorded at five temperatures in the range  $250 - 350^\circ\text{C}$ .

Solubility Measurements. Approximately 1, 2 (series A) or 10 (series B) g of  $\text{Ag}_2\text{MoO}_4$ , 75g of  $(\text{K,Na})\text{NO}_3$  and varying amounts of  $\text{Na}_2\text{MoO}_4$  or  $\text{AgNO}_3$  were equilibrated at  $280^\circ\text{C}$  under stirring for at least 50 h. When  $\text{Na}_2\text{MoO}_4$  was added a corresponding amount of  $\text{KNO}_3$  was also added in order to keep the total ratio  $\text{Na}:\text{K}$  constant at 1.00 in all systems. Maximum concentrations were  $0.12 \text{ mol kg}^{-1}$   $\text{Na}_2\text{MoO}_4$  and  $0.4 \text{ mol kg}^{-1}$   $\text{AgNO}_3$ . Samples from the nitrate melt were analysed for silver and molybdate. Total molybdate was determined in water solutions by a colorimetric method employing mercaptoacetic acid.<sup>12</sup> Before the analysis silver was removed from the solutions by precipitation as  $\text{AgBr}$ .

Silver was determined by electroanalytical precipitation of Ag on a rotating platinum cathode from hot aqueous cyanide solutions. In series B the composition of the solid phase could be calculated from the difference between added and found amounts of various ions in the nitrate melt after equilibration.

### Results from Potentiometric Measurements

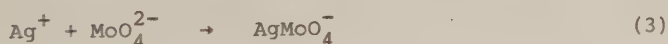
The emf of the cell at the molybdate concentration considered minus the emf at  $C_{Mo} = 0$ ,  $\Delta E$ , is related to the concentrations of free silver and molybdate ions in the melt by

$$\exp \left( \frac{F}{R} \frac{\Delta E}{T} \right) = 1 + \sum_{\underline{m}} \sum_{\underline{n}} \underline{m} \underline{\beta}_{\underline{mn}} [Ag^+]^{\underline{m}-1} [MoO_4^{2-}]^{\underline{n}} \quad (2)$$

where  $\underline{\beta}_{\underline{mn}}$  are the stability constants<sup>2</sup> for the different silver molybdate complexes,  $Ag_{\underline{m}}(MoO_4)_{\underline{n}}^{(2\underline{n}-\underline{m})-}$ . Diffusion potentials and changes in activity coefficients are negligible in dilute ionic solutions of this kind.<sup>9</sup> The left hand member of equation (2) could be best described with a second degree polynomial in  $[MoO_4^{2-}]$  ( $\underline{n} = 1$  and  $2$ ) independent of  $C_{Ag}$ . The independence of central ion concentration indicates  $\underline{m} = 1$  for all complex species, i. e. only  $AgMoO_4^-$  and  $Ag(MoO_4)_2^{3-}$  are present in measurable amounts.

Two titrations at  $280^\circ C$  with different  $C_{Ag}$  are shown in Fig 1. The final set of stability constants was obtained by use of a computer program which minimizes the sum of squared errors  $(\Delta E_{obs} - \Delta E_{calc})^2$  according to equation (2). Table 1 gives stability constants from emf measurements at five temperatures and the number of melt compositions studied at each temperature.

The thermodynamic parameters  $\Delta H_1^O$  and  $\Delta S_1^O$  for the simplified reaction



were estimated. As  $-RT \ln \beta_{11}$ , within estimated errors, is a linear function of temperature,  $\Delta H_1^O$  and  $\Delta S_1^O$  were determined by linear regression analysis. Each datum was given a weight proportional to  $(\sigma_1(T))^{-2}$ , where  $\sigma_1(T)$  is given by

$$\sigma_1(T) = RT \frac{\sigma(\beta_{11})}{\beta_{11}} \quad (4)$$

Here  $\sigma(\beta_{11})$  is the estimated standard deviation in  $\beta_{11}$  at the temperature in question. The standard state relates to unity ionic fractions. The above calculations give  $\Delta H_1^O = -7.5 \pm 1.6$  kJ mol<sup>-1</sup> and  $\Delta S_1^O = 20 \pm 3$  J mol<sup>-1</sup> K<sup>-1</sup>. Stated errors are one estimated standard deviation.

### Results from Solubility Measurements

The solid phase. When solid Ag<sub>2</sub>MoO<sub>4</sub> was equilibrated with molten 1:1 (K,Na)NO<sub>3</sub> containing various amounts of molybdate, it appeared that the ratio of Ag<sup>+</sup> to MoO<sub>4</sub><sup>2-</sup> in the solid was less than 2. Furthermore, this ratio decreased monotonously as  $C_{MO}$  was increased. No irregularities that might indicate phase transitions - as in the corresponding CrO<sub>4</sub><sup>2-</sup> system<sup>5</sup> - could be detected. From experiments with pure NaNO<sub>3</sub> and pure KNO<sub>3</sub> as solvents at 350°C it was concluded that solid Ag<sub>2</sub>MoO<sub>4</sub> dissolves Na<sub>2</sub>MoO<sub>4</sub> but not K<sub>2</sub>MoO<sub>4</sub>.

At 553 K the stable form of Ag<sub>2</sub>MoO<sub>4</sub> is the  $\beta$ -phase.<sup>11</sup> Na<sub>2</sub>MoO<sub>4</sub> crystallizes in the so-called low-temperature modification IV below 717 K.<sup>13</sup> This modification is isostructural with  $\beta$ -Ag<sub>2</sub>MoO<sub>4</sub>, crystallizing in the cubic spinel type space group Fd3m - O<sub>h</sub><sup>7</sup>. The edge lengths of the unit cell have been reported to be

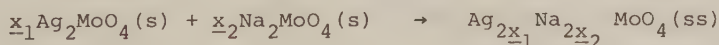
9.322 Å for  $\text{Ag}_2\text{MoO}_4$ <sup>11</sup> and 9.108 Å for  $\text{Na}_2\text{MoO}_4$ <sup>14</sup> at room temperature. We recorded power X-ray photographs at 298 K of pure  $\text{Ag}_2\text{MoO}_4$ , pure  $\text{Na}_2\text{MoO}_4$  and one preparation from the solid-melt equilibration studies, assumed to be a solid solution  $(\text{Ag},\text{Na})_2\text{MoO}_4$  with the fraction of  $\text{Ag}_2\text{MoO}_4$ ,  $x_1 = 0.67$ . Edge lengths of 9.316(1) Å and 9.102(1) Å for  $\text{Ag}_2\text{MoO}_4$  and  $\text{Na}_2\text{MoO}_4$  were obtained in good agreement with literature data.<sup>11,14</sup> For the solid solution only minor shifts in the diffraction lines were observed, yielding an edge length of 9.246(1) Å, which compares well with the calculated weighted average for the pure components, 9.245 Å.

The thermodynamic activity  $a_1$  of  $\text{Ag}_2\text{MoO}_4$  in the solid solution can be calculated if the composition of both solid and liquid phases are known in a suitable concentration range. It holds<sup>6</sup>,

$$a_{1j} = \exp \left[ \int_{\ln R_0}^{\ln R_j} (x_1^{-1} - 1) d \ln R \right] \quad (5)$$

where  $R = (y_-^2 \cdot [\text{MoO}_4^{2-}])^{-1}$  and  $y = [\text{Na}^+]/([\text{Na}^+] + [\text{K}^+] + [\text{Ag}^+])$ .

The index  $j$  is used to denote quantities referring to the same actual system and  $R_0$  refers to a system with  $x_1 = 1$  and  $a_1 = 1$  i.e. the standard state chosen for  $\text{Ag}_2\text{MoO}_4$ . Activities determined in this way from experimental solubility data of series B are plotted against the mole fraction of  $\text{Na}_2\text{MoO}_4$ ,  $x_2$ , in Fig 2. It is readily seen that the experimentally obtained  $a_1$  values deviate significantly from the ideal Temkin relation  $a_1 = x_1^2$ , corresponding to a random distribution of  $\text{Na}^+$  and  $\text{Ag}^+$  on a cation sublattice with  $\Delta H_{\text{mix}} = 0$  for the mixing process



This deviation can, however, be well accounted for by treating the solids as regular solutions, i.e. with nonzero  $\Delta H_{\text{mix}}$  but ideal  $\Delta S_{\text{mix}}$ , referring to a cation mixing only. It should thus hold  $\frac{RT}{A} \ln f_1 = \frac{A}{x_2^2}$ , where  $f_1$  is the activity coefficient for  $\text{Ag}_2\text{MoO}_4$  related to the ideal mixing model, i.e.  $f_1 = a_1 x_1^{-2}$ , and  $A$  is the interaction parameter. The ratio  $\ln f_1 / x_2^2$  is found to be constant for  $x_2^2 > 0.03$ , yielding  $A = (2.1 \pm 0.1) \frac{RT}{A} = (9.6 \pm 0.5)$

$\text{kJ mol}^{-1}$ . In Fig 3  $\ln f_1$  is shown as a function of  $x_2^2$ . The deviations from the straight line for the smallest values of  $x_2$  are probably due to some minor systematic termination error in the integration process according to equation (5).

An equilibrium constant,  $K_{\text{Na}}$ , for the process



was independently determined from molybdate analyses of a melt equilibrated with solid  $\text{Na}_2\text{MoO}_4$ , resulting in  $K_{\text{Na}} = 0.042 \pm 0.001 \text{ mol kg}^{-1}$ .

For systems with solid solutions  $(\text{Ag}, \text{Na})_2\text{MoO}_4$  as solid phase the regular solution model gives

$$K_{\text{Na}} = \gamma^2 \cdot [\text{MoO}_4^{2-}] / x_2^2 \exp(\underline{A} x_1^2 / RT) \quad (7)$$

where the denominator is the activity of  $\text{Na}_2\text{MoO}_4$  in the solid solution. In Fig 4 experimental quantities  $\gamma^2 \cdot [\text{MoO}_4^{2-}] \cdot x_2^{-2}$  are plotted against  $x_2$  and compared to the theoretical curve  $f(x_2) = K_{\text{Na}} \exp(\underline{A} x_1^2 / RT)$  with the independently determined  $K_{\text{Na}} = 0.042 \text{ mol kg}^{-1}$  and  $\underline{A} = 9.6 \text{ kJ mol}^{-1}$ . The good agreement suggests that the  $(\text{Ag}, \text{Na})_2\text{MoO}_4$  solids probably can be treated as regular solutions over the whole composition range as indicated by the extended curves of Fig 2.

Complexation in the range  $2 C_{\text{Mo}} > C_{\text{Ag}}$ . Fig 5 surveys all experimental solubility data.

Although the over-all ratio  $\text{Na}:\text{K}$  was adjusted to be 1 in all systems, it is obvious that the solid solution formation makes this ratio less than 1 in the melts. The lowest value is 0.97 in series A and 0.82 in series B. No significant difference in the solubilities from series A and B could be detected, however, so all data were used simultaneously in the computation of equilibrium constants. The relation between  $C_{\text{Ag}}$ ,  $[\text{Ag}^+]$  and  $[\text{MoO}_4^{2-}]$

in the melts is

$$\underline{C}_{\text{Ag}} [\text{MoO}_4^{2-}]^{\frac{1}{2}} \underline{a}_1^{-\frac{1}{2}} = \frac{1}{\underline{K}_s} (1 + \sum_{\underline{m}} \sum_{\underline{n}} \underline{\beta}_{\underline{mn}} [\text{Ag}^+]^{\underline{m}-1} [\text{MoO}_4^{2-}]^{\underline{n}}) \quad (8)$$

where  $\underline{K}_s$  is the equilibrium constant for



No polynuclear complexes could be detected in this composition range by emf measurements. Hence, the solubility data were analysed assuming  $\underline{m} = 1$  only. Actually, it would be quite sufficient to take only  $\text{AgMoO}_4^-$  into consideration in an explanation of the shape of the solubility curve within the limits of experimental errors. Since, however, a small but significant fraction of  $\text{Ag(I)}$  was found to be present as  $\text{Ag}(\text{MoO}_4)_2^{3-}$  in unsaturated melts, the left hand member of equation (8) was rigorously treated as a second degree polynomial in  $[\text{MoO}_4^{2-}]$ . In this way  $\underline{K}_s$ ,  $\underline{\beta}_{11}$  and  $\underline{\beta}_{12}$  were estimated, but the existence of  $\text{Ag}(\text{MoO}_4)_2^{3-}$  is of course by no means proven by the solubility data.

The results are found in table 2.

Complexation in the range  $\underline{C}_{\text{Ag}} > 2 \underline{C}_{\text{Mo}}$ . In analogy with equation (8):

$$\underline{C}_{\text{Mo}} [\text{Ag}^+]^2 \underline{a}_1^{-1} = \underline{K}_s (1 + \sum_{\underline{m}} \sum_{\underline{n}} \underline{n} \underline{\beta}_{\underline{mn}} [\text{Ag}^+]^{\underline{m}} [\text{MoO}_4^{2-}]^{\underline{n}-1}) \quad (10)$$

It should be noted that variations in  $\underline{a}_1$  have to be considered in this composition range too.  $\underline{a}_1$  is in fact effectively 1 only for  $\underline{C}_{\text{Ag}} > 0.3 \text{ mol kg}^{-1}$  in the melt. In the range  $\underline{C}_{\text{Ag}} > 2 \underline{C}_{\text{Mo}}$  the species  $\text{Ag}^+$ ,  $\text{MoO}_4^{2-}$  and  $\text{AgMoO}_4^-$  can not explain the shape of solubility curve alone. The experimental data  $\underline{C}_{\text{Mo}} [\text{Ag}^+]^2 \underline{a}_1^{-1}$  are, however, well described by a second degree polynomial in  $[\text{Ag}^+]$  which indicates that a complex of composition  $\text{Ag}_{2\underline{n}}(\text{MoO}_4)_{\underline{n}}$  must be considered. The simplest and most probable species is one with the formal composition  $\text{Ag}_2\text{MoO}_4$ .

Least squares estimates of  $K_s$ ,  $\beta_{11}$  and  $\beta_{21}$  are given in table 2.

## Discussion

From the comparison in table 2 of equilibrium constants obtained by the two methods it is quite clear that solubility measurements give rather poor estimates of the  $\beta$  values. An eventual difference due to the fact that solubility data actually refer to melts with a slight excess of  $K^+$  over  $Na^+$ , whereas emf data refer to melts with a slight excess of  $Na^+$  over  $K^+$  - is obscured by the wide limits of uncertainty in the  $\beta$  values from solubility measurements. The reason for these wide limits is of course to be found in the weak complexation; note that  $K_s$  is obtained with good accuracy from both branches of the solubility curve.

Fig 6 shows the fraction  $\alpha$  of silver present as  $Ag^+$ ,  $AgMoO_4^-$  and  $Ag(MoO_4)_2^{3-}$  as a function of  $[MoO_4^{2-}]$  at the two extreme temperatures 524 K and 622 K. Like the  $Ag(I)$  association with  $IO_3^-$  and  $CrO_4^{2-}$  the total molybdate complexation of silver does not change very much with temperature. The existence of  $Ag(MoO_4)_2^{3-}$  may of course be questioned at the higher temperatures, but this complex can certainly not be omitted in a proper description of the system at the lower temperatures. The importance of  $Ag(MoO_4)_2^{3-}$  at the lower temperatures can also be demonstrated by a comparison between  $\beta_{11}$  values obtained by us and by Sacchetto and coworkers,<sup>4</sup> neglecting  $Ag(MoO_4)_2^{3-}$ . They agree fairly well for  $T > 553$  K, but below this temperature our values are significantly smaller.

Comparing  $MoO_4^{2-}$  and  $CrO_4^{2-}$  as ligands for  $Ag^+$  in  $(K,Na)NO_3$  melts one can say that the same species seem to be formed, but the over-all complexation is somewhat weaker in the chromate system.

$\Delta H_{-1}^O$  and  $-T\Delta S_{-1}^O$  give comparable contributions to  $\Delta G_{-1}^O$  for formation of  $\text{AgMoO}_4^-$  in both systems.  $\Delta S_{-1}^O$  appears to be the same,  $20 \pm 3 \text{ J K}^{-1} \text{ mol}^{-1}$  for the two ligands, and it seems that the difference in  $\beta_{11}$  is mainly caused by the more exothermal nature of the  $\text{MoO}_4^{2-}$  association, which in turn might imply a slightly stronger Ag - O interaction in  $\text{AgMoO}_4^-$ .

The discovery of a wide range of regular  $(\text{Ag,Na})_2\text{MoO}_4$  solid solutions is in accordance with the statements of Belyaev and Doroshenko.<sup>7</sup> The binary system  $\text{Ag}_2\text{MoO}_4$  -  $\text{Na}_2\text{MoO}_4$  is certainly not a simple entectic one. In contrast to  $(\text{Ag,Na})_2\text{MoO}_4$  solid solutions the analogous  $(\text{Ag,Na})_2\text{CrO}_4$  solids were found to exhibit ideal Temkin behaviour in the range  $x_2 \leq 0.2$  where they have the  $\text{Ag}_2\text{CrO}_4$  structure, though  $\text{Na}_2\text{CrO}_4$  and  $\text{Ag}_2\text{CrO}_4$  are not isostructural. The importance of structural similarities between the compounds is, however, best visualized by a comparison between the ion exchange constants  $K$  for the equilibria



between solids and nitrate melts. The values  $p(K/\text{mol}^2\text{kg}^{-2}) = 5.1$  for  $\text{M} = \text{Cr}^5$  and 4.3 for  $\text{M} = \text{Mo}$  are obtained from  $K_{\text{S}}$  and  $K_{\text{Na}}$  for the two systems at 553 K when the standard state for solid  $\text{Na}_2\text{CrO}_4$  is chosen to be the hypothetical pure  $\text{Na}_2\text{CrO}_4$  with  $\text{Ag}_2\text{CrO}_4$  structure.

The experimental assistance by Dr. Ghazi Noori is gratefully acknowledged. This study has been supported by a grant from Swedish Natural Science Research Council.

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Table 1. The over-all stability constants  $\beta_{11}$  and  $\beta_{12}$  for  $\text{Ag}^+ - \text{MoO}_4^{2-}$  complexes in molten 1:1 (K,Na) $\text{NO}_3$  from emf measurements. The limits of error are 95% confidence limits.  $\underline{N}$  = number of melt compositions studied.

| $\underline{T}/\text{K}$ | $\beta_{11}/\text{mol}^{-1}\text{kg}$ | $\beta_{12}/\text{mol}^{-2}\text{kg}^2$ | $\underline{N}$ |
|--------------------------|---------------------------------------|-----------------------------------------|-----------------|
| 524                      | $5.6 \pm 0.2$                         | $18 \pm 3$                              | 30              |
| 538                      | $5.5 \pm 0.2$                         | $13 \pm 2$                              | 16              |
| 553                      | $5.2 \pm 0.2$                         | $10 \pm 3$                              | 40              |
| 588                      | $5.0 \pm 0.2$                         | $4 \pm 3$                               | 16              |
| 622                      | $4.1 \pm 0.1$                         | $6 \pm 1$                               | 56              |

Table 2. Stability constants and  $\underline{K}_s$  for  $\text{Ag}_2\text{MoO}_4$  in 1:1 (K,Na) $\text{NO}_3$  at  $280^\circ\text{C}$  determined by different experimental methods. The errors are 95% confidence limits.  $\underline{N}$  = number of melt compositions studied.

| $0^6/\text{mol}^3\text{kg}^{-3}$ | $\beta_{11}/\text{mol}^{-1}\text{kg}$ | $\beta_{12}/\text{mol}^{-2}\text{kg}^2$ | $\beta_{21}/\text{mol}^{-2}\text{kg}^2$ | $\underline{N}$ | Method                                                       |
|----------------------------------|---------------------------------------|-----------------------------------------|-----------------------------------------|-----------------|--------------------------------------------------------------|
| 0.1                              | $8 \pm 2$                             | -                                       | $16 \pm 6$                              | 15              | sol $\underline{C}_{\text{Ag}} > 2\underline{C}_{\text{Mo}}$ |
| 0.2                              | $3 \pm 3$                             | ( $2 \pm 23$ )                          | -                                       | 24              | sol $2\underline{C}_{\text{Mo}} > \underline{C}_{\text{Ag}}$ |
|                                  | $5.2 \pm 0.2$                         | $10 \pm 3$                              |                                         | 40              | emf                                                          |

Figure legends.

Figure 1.  $\frac{C_{Ag}}{[Ag^+]}$  versus  $[MoO_4^{2-}]$  from two emf titrations at different  $\frac{C_{Ag}}{[Ag^+]}$  in 1:1 (K,Na)NO<sub>3</sub> at 553 K.  $\frac{C_{Ag}}{[Ag^+]} = 9.45 \cdot 10^{-4}$  mol kg<sup>-1</sup> (□) and  $\frac{C_{Ag}}{[Ag^+]} = 5.29 \cdot 10^{-4}$  mol kg<sup>-1</sup> (○).

Figure 2. Activity - composition relations for solid solutions (Ag,Na)<sub>2</sub>MoO<sub>4</sub> at 553 K. Experimental activities (○),  $\underline{a}_i$  from the regular solution model with  $\underline{A} = 9.6$  kJ mol<sup>-1</sup> (~), and  $\underline{a}_i = \underline{x}_i^2$  (i = 1 and 2) according to an ideal cationic mixing model (- - -).

Figure 3. Logarithm of the activity coefficient  $\underline{f}_1$  for Ag<sub>2</sub>MoO<sub>4</sub> in solid solutions (Ag,Na)<sub>2</sub>MoO<sub>4</sub> at 553 K versus the square of the mole fraction of Na<sub>2</sub>MoO<sub>4</sub>,  $\underline{x}_2^2$ . The slope of the straight line is 2.1.

Figure 4. Experimental values  $\gamma^2[MoO_4^{2-}]\underline{x}_2^{-2}$  for solid solutions (Ag,Na)<sub>2</sub>MoO<sub>4</sub> in equilibrium with molten 1:1 (K,Na)NO<sub>3</sub> at 553 K. The graph is  $f(\underline{x}_2) = \underline{K}_{Na} \exp \left( \frac{\underline{A}\underline{x}_1^2}{RT} \right)$  with  $\underline{K}_{Na} = 0.042$  mol kg<sup>-1</sup> and  $\underline{A} = 9.6$  kJ mol<sup>-1</sup>.

Figure 5. Solubility curve for Ag<sub>2</sub>MoO<sub>4</sub> in molten 1:1 (K,Na)NO<sub>3</sub> at 553 K.

Figure 6. The fraction  $\underline{a}$  of Ag(I) present in different species in molten 1:1 (K,Na)NO<sub>3</sub> at 524 K and 622 K as a function of  $[MoO_4^{2-}]$  in the limit  $\frac{C_{Ag}}{[Ag^+]} \rightarrow 0$ . The graphs are calculated from the constants of table 1.

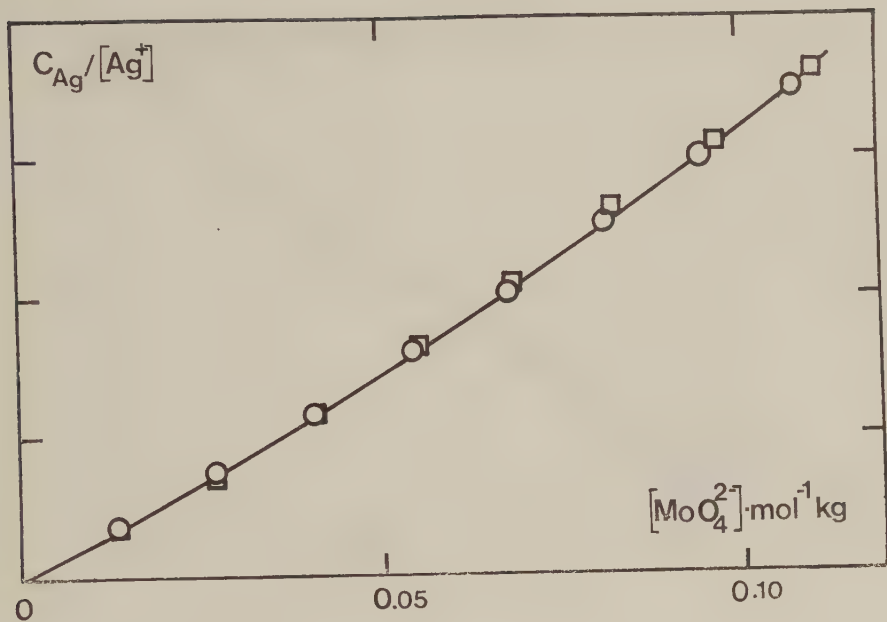


Figure 1

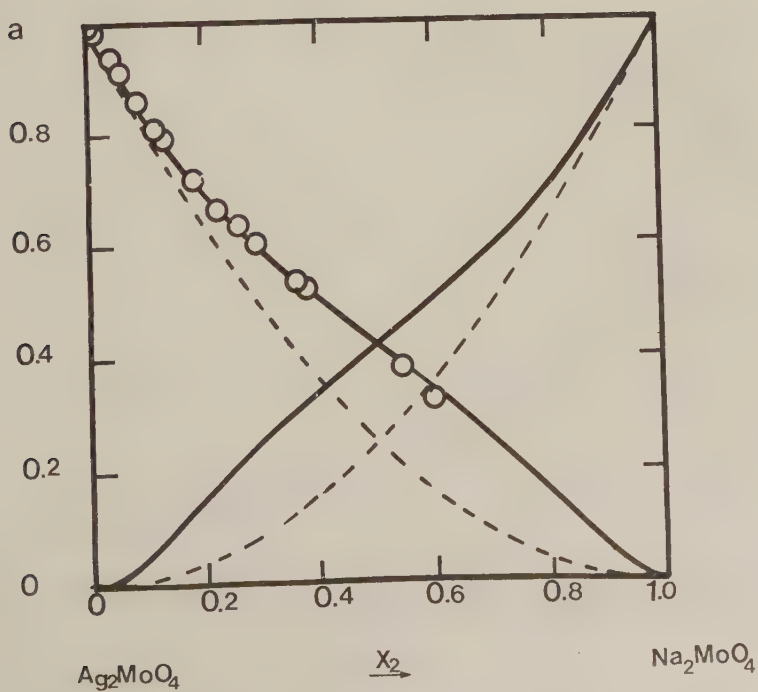


Figure 2

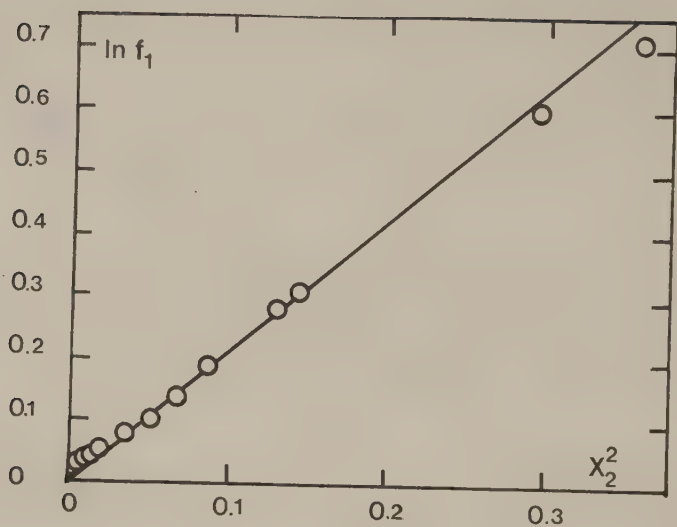


Figure 3

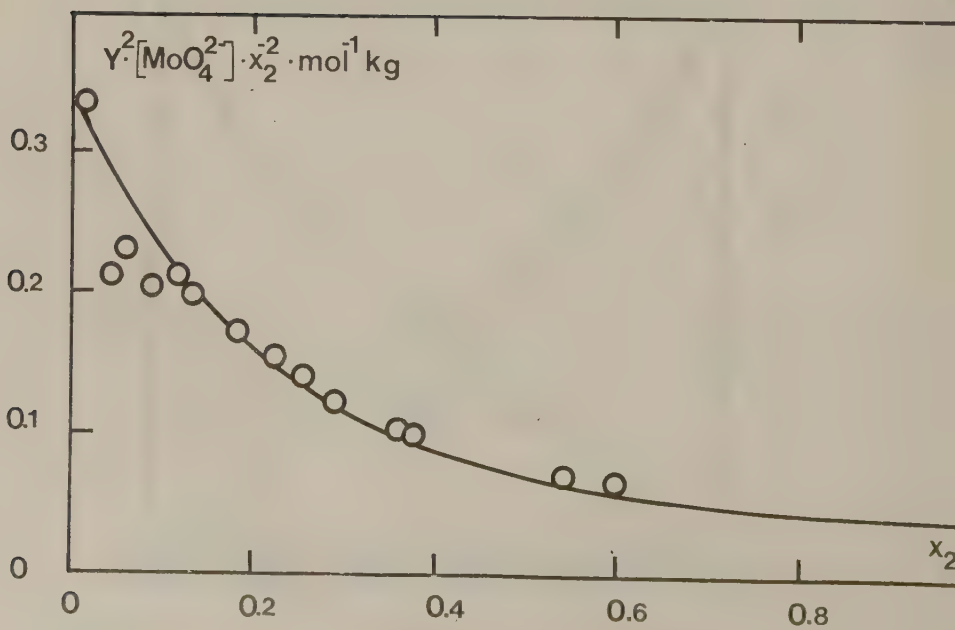


Figure 4

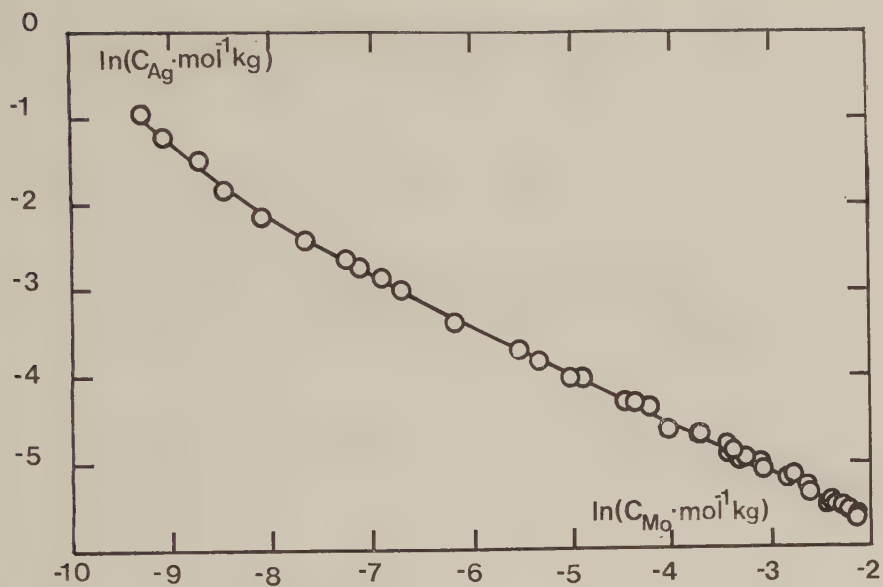


Figure 5

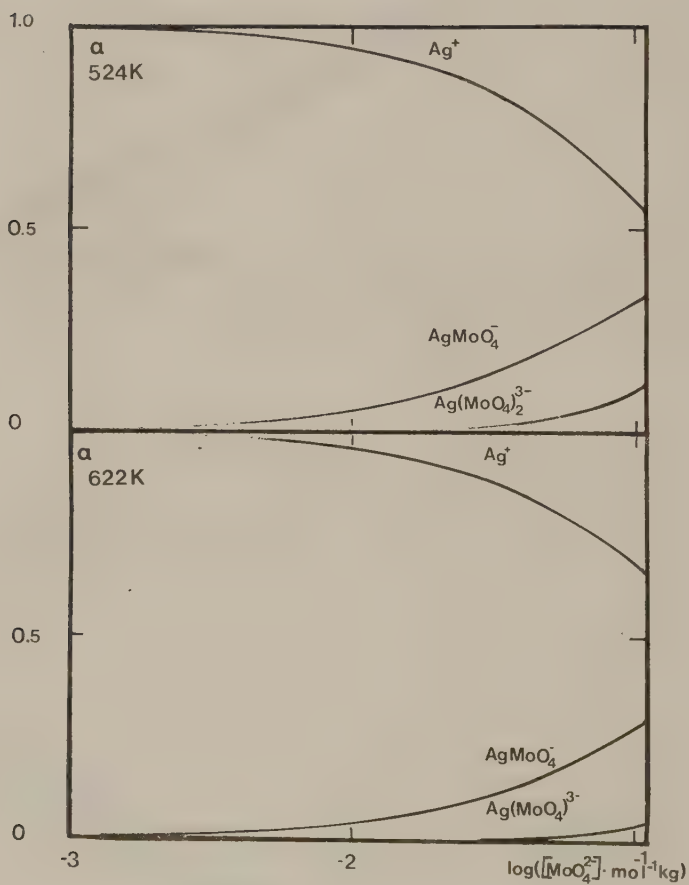


Figure 6

Received:

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Complex Formation between  $\text{Ag}^+$  and  $\text{PO}_4^{3-}$  in Molten Equimolar  $(\text{K},\text{Na})\text{NO}_3$ . A Comparison with Other Silver(I) Oxoanion Complexes in the same Medium.

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The complex formation between  $\text{Ag}(\text{I})$  and orthophosphate ions in molten 1:1  $(\text{K},\text{Na})\text{NO}_3$  has been examined by potentiometry and solubility measurements. Stability constants for the complexes  $\text{AgPO}_4^{2-}$  and  $\text{Ag}_2\text{PO}_4^-$  have been estimated from potentiometric data in the range 524 K - 622 K. These constants can not be independently determined from solubility measurements, but it is shown that the solubility data, recorded at 553 K, are consistent with the complexation model inferred from the potentiometric study. A continuous range of solid solutions  $(\text{Ag},\text{Na})_3\text{PO}_4$  has been discovered.

From the temperature dependence of  $\beta_{11}$ , <sup>the stability constant,</sup> values for  $\Delta H_1^\circ$  and  $\Delta S_1^\circ$  of the process  $\text{Ag}^+ + \text{PO}_4^{3-} \rightarrow \text{AgPO}_4^{2-}$  have been estimated. These parameters are compared to the corresponding ones for the formation of  $\text{AgNO}_2$ ,  $\text{AgIO}_3$ ,  $\text{AgClO}_4^-$  and  $\text{AgMoO}_4^-$  in the same medium, previously determined by us, and the general trends in the values are briefly discussed.

(complexes)

The stability of silver(I) with nitrite,<sup>1</sup> iodate,<sup>2</sup> chromate<sup>3</sup> and molybdate<sup>4</sup> in molten 1:1 (K,Na)NO<sub>3</sub> have been studied previously at our laboratory mainly by solubility and emf measurements. In an ionic solvent like (K,Na)NO<sub>3</sub> the complex formation reaction can be regarded as an exchange of an alkali ion in the coordination shell of the oxoanion for a silver ion. Hence, it might be informative to study an oxoanion of even higher anionic charge, such as PO<sub>4</sub><sup>3-</sup>, in order to examine the effects of ligand charge on the complex formation.

Metal complexes of PO<sub>4</sub><sup>3-</sup> have not been studied in molten salts prior to this work, but two studies on depolymerization of condensed phosphates in molten alkali nitrate media, emphasizing the effects of various alkali metal ions on the depolymerization reactions, have appeared.<sup>5,6</sup>

From water solution chemistry metal complexes with orthophosphate are well established although nothing seems to be reported on silver complexes. Waki and Nakashima have, however, recently described silver complexes of polymer phosphorous oxoanions with ring structure.<sup>7</sup>

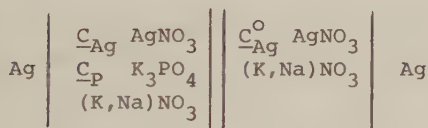
Solid silver oxoanion salts in equilibrium with (K,Na)NO<sub>3</sub> melts have previously been found to dissolve alkali salts from the melt.<sup>2,3,4</sup> In the present case solid solutions (Ag,Na)<sub>3</sub>PO<sub>4</sub> have been examined and characterized in connexion with solubility measurements at 553 K, the original aim of which was to determine complex stabilities by an independent experimental method. It soon turned out, however, that reliable estimates of stability constants could only be obtained from emf measurements.

## Experimental

Chemicals.  $\text{NaNO}_3$ ,  $\text{KNO}_3$  and  $\text{AgNO}_3$  (Merck p.a.) were preconditioned and stored as described elsewhere.<sup>8</sup>  $\text{K}_3\text{PO}_4$  (Mallinckrodt, analytical reagent) was dried in several steps at successively higher temperatures from 393 K to 773 K and then at 473 K under vacuum for several days.  $\text{Ag}_3\text{PO}_4$  was precipitated from hot neutralised aqueous solutions of  $\text{K}_3\text{PO}_4$  and  $\text{AgNO}_3$  and dried at 423 K prior to use. The purity was checked by analysis for Ag. Result: theoretical Ag, 77.3%, found 77.2%.

Apparatus. The equipment used for solubility and emf measurements has been described elsewhere.<sup>1,8,9</sup>

Emf measurements. The following cell was used:



test melt      reference melt

In each series the test melt contained 250 g equimolar  $(\text{K,Na})\text{NO}_3$  and a fixed total concentration of  $\text{Ag(I)}$  varying between  $0.6 \times 10^{-3}$  and  $1.6 \times 10^{-3} \text{ mol kg}^{-1}$  in different runs. After equilibration for at least 18 h the melt was titrated with  $\text{K}_3\text{PO}_4$ . The maximum phosphate concentration was as low as  $8 \times 10^{-4} \text{ mol kg}^{-1}$  in order to prevent precipitation of  $\text{Ag}_3\text{PO}_4$ . (Note that the solubility of alkali phosphate is remarkably low, about  $2.3 \times 10^{-3} \text{ mol kg}^{-1}$  at 553 K) To make the additions easy to handle a 1:10 mixture of  $\text{K}_3\text{PO}_4$  and  $(\text{K,Na})\text{NO}_3$  was used as titrant. The extra  $(\text{K,Na})\text{NO}_3$  added by this procedure was less than 0.5 g (0.2%) in one titration series and the decrease in  $\underline{C}_{\text{Ag}}$  brought about in this way has been neglected in the calculations. Stable emfs were attained within 30 min. Data were recorded at five temperatures between 523 and

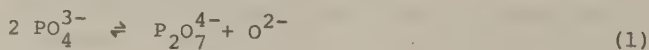
623 K. Table 1 gives the number of melt compositions studied at each temperature.

Solubility measurements. Systems containing 75.00 g of equimolar (K,Na)NO<sub>3</sub>, 4 g of Ag<sub>3</sub>PO<sub>4</sub> and varying amounts of AgNO<sub>3</sub> or K<sub>3</sub>PO<sub>4</sub> were agitated for at least 100 h at 553 K until equilibrium was attained (as concluded from constant solubility). Quenched samples were analysed for silver and phosphate in water solutions. Total phosphate was determined photometrically according to the molybdenum blue method with SnCl<sub>2</sub> as reductant.<sup>10</sup> This method is sensitive only to orthophosphate and not to diphosphate. Prior to the analysis Ag<sup>+</sup> was removed by precipitation as AgBr and filtration. Total silver was determined by electroanalytical precipitation of Ag on a rotating platinum cathode from hot aqueous cyanide solutions. The composition of the solid phase was calculated from the difference between added and found amounts of K<sub>3</sub>PO<sub>4</sub> or AgNO<sub>3</sub> in the nitrate melt.

#### The stability of PO<sub>4</sub><sup>3-</sup> and P<sub>2</sub>O<sub>7</sub><sup>4-</sup>.

Recently Copeland et.al.<sup>5,6</sup> reported that the degradation of higher polyphosphates proceeds readily to orthophosphate in nitrate melts containing an excess of Li<sup>+</sup> whereas P<sub>2</sub>O<sub>7</sub><sup>4-</sup> was the final breakdown product in nitrate melts with alkali ions of less polarizing power.

Shams El Din and Gerges<sup>18</sup> determined the equilibrium constant K for the condensation reaction



in pure KNO<sub>3</sub> at 623 K. They found K = 1.5 x 10<sup>-6</sup>. In order to test the effect of Ag(I) being present in the melts, we

prepared two (K,Na)NO<sub>3</sub> melts with P<sub>2</sub>O<sub>7</sub><sup>4-</sup>: one containing 0.07 mol kg<sup>-1</sup> AgNO<sub>3</sub> and the other one without AgNO<sub>3</sub>. In the silver containing melt 70% of the total phosphate was degraded to PO<sub>4</sub><sup>3-</sup> while in the other one only 40% was degraded after equilibrium was attained. This experiment indicates that Ag<sup>+</sup>, even in rather low concentrations, has an effect similar to that of Li<sup>+</sup>; PO<sub>4</sub><sup>3-</sup> is stabilized. Furthermore the combination of Na<sup>+</sup> and K<sup>+</sup> in the solvent has an effect in the same direction.

Although the dissociation reaction studied here is not the reversal of process (1) but rather something like



it is highly probable that the fraction of P<sub>2</sub>O<sub>7</sub><sup>4-</sup> formed from added PO<sub>4</sub><sup>3-</sup> in our (K,Na)NO<sub>3</sub> melts containing AgNO<sub>3</sub> is smaller than 0.2%. This number is calculated for our maximum  $\underline{C}_P$  by use of  $\underline{K} = 1.5 \times 10^{-6}$  for reaction (1) in pure KNO<sub>3</sub> at 350°C.

In another experiment 2 g of solid Ag<sub>3</sub>PO<sub>4</sub> was equilibrated with 75 g of the more acidic molten eutectic (K,Li)NO<sub>3</sub> (containing 43% Li<sup>+</sup>) at 433 K. To our surprise all the green Ag<sub>3</sub>PO<sub>4</sub> was dissolved and a white precipitate, probably Li<sub>3</sub>PO<sub>4</sub>, was formed. All added silver was found by analysis in the liquid phase, which had a PO<sub>4</sub><sup>3-</sup> content of about 10<sup>-4</sup> mol kg<sup>-1</sup>. These qualitative observations may be taken as an indication of a pronounced selective Li<sup>+</sup> solvation of PO<sub>4</sub><sup>3-</sup> even at high Ag(I) concentrations ( $\underline{C}_{Ag} = 0.192$  mol kg<sup>-1</sup>). It is thus evident that the cationic composition of the alkali nitrate solvent may have a profound influence on the complexation reactions studied.

## Potentiometric Measurements.

From stoichiometric requirements:

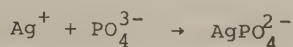
$$\underline{C}_{\text{Ag}}/[\text{Ag}^+] = 1 + \sum_m \sum_n m \beta_{mn} [\text{Ag}^+]^{m-1} [\text{PO}_4^{3-}]^n \quad (3)$$

where  $\beta_{mn}$  are the stability constants of the silver phosphate complexes  $\text{Ag}_m(\text{PO}_4)_n^{(3n-m)-}$ . As junction potentials are negligible in these dilute melts

$$\Delta \underline{E} = \frac{RT}{F} \ln (\underline{C}_{\text{Ag}}/[\text{Ag}^+]) \quad (4)$$

where  $\underline{E}$  is the emf at the phosphate concentration considered minus the emf at  $\underline{C}_P = 0$ .  $\underline{C}_{\text{Ag}}/[\text{Ag}^+]$  was found to be dependent on the total silver content of the melt (cf. Fig 1). From a preliminary graphical data analysis it was concluded that a complex of the form  $\text{Ag}_2\text{PO}_4^-$  is formed besides  $\text{AgPO}_4^{2-}$ . In the final treatment of data a computer program which minimizes the sum of squared errors  $(\Delta \underline{E}_{\text{obs}} - \Delta \underline{E}_{\text{calc}})^2$  according to eqns. (3) and (4) was used. Table 1 gives stability constants  $\beta_{11}$  and  $\beta_{21}$  at five temperatures.

From the temperature dependence of the free energy change of the simplified reaction



the enthalpy and entropy contributions have been estimated. The standard state chosen relates to unity ionic fractions.  $\Delta \underline{H}_1^{\circ}$  and  $\Delta \underline{S}_1^{\circ}$  have been estimated by linear regression with a weight scheme analogous to the one described in a previous paper.<sup>1</sup>

The resulting parameters are  $\Delta \underline{H}_1^{\circ} = -12 \pm 7 \text{ kJ mol}^{-1}$  and  $\Delta \underline{S}_1^{\circ} = 33 \pm 12 \text{ J mol}^{-1} \text{ K}^{-1}$ . Stated errors are one estimated standard deviation. Obviously, the precision in primary data does only allow very crude estimates of  $\Delta \underline{H}_1^{\circ}$  and  $\Delta \underline{S}_1^{\circ}$ .

## Solubility Measurements.

From experiments with solids and nitrate melts with different cationic composition it was concluded that an exchange reaction



between melt and solid phase occurs. Fig 2 shows mole fraction of  $\text{Na}_3\text{PO}_4$ ,  $\underline{x}_2$ , in the solid phase as a function of  $\underline{C}_p$ . The very rapid change at  $\underline{C}_p \approx 9 \cdot 10^{-4} \text{ mol kg}^{-1}$  probably forebodes a phase transition in the solid.

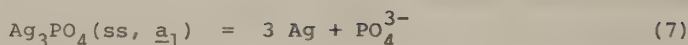
The activity  $\underline{a}_1$  of  $\text{Ag}_3\text{PO}_4$  in the solid phase was determined according to

$$\underline{a}_{1j} = \exp \left( \int_{\ln \underline{R}_0}^{\ln \underline{R}_j} (\underline{x}_2/\underline{x}_1) d \ln \underline{R} \right) \quad (6)$$

where  $\underline{R} = (\underline{y}^3 \cdot [\text{PO}_4^{3-}])^{-1}$ ,  $\underline{y} = [\text{Na}^+]/([\text{Na}^+] + [\text{K}^+])$  and  $\underline{x}_1$  is the mole fraction of  $\text{Ag}_3\text{PO}_4$  in the solid phase.<sup>11,12</sup> The index  $j$  is used to denote different quantities referring to the same actual system.  $\underline{R}_0$  refers to a system with  $\underline{x}_1 = 1$  and  $\underline{a}_1 = 1$ . Since no such system could be studied experimentally, a starting point for the integration (i.e. the standard state) had to be found by extrapolation. This was done indirectly in the following way. Quantities  $\ln(\underline{a}_{1j}/\underline{a}_1^*)$  were determined by direct integration according to eqn. (6) with  $\underline{a}_1$  referring to the solid solution with the highest  $\underline{x}_1 (=0.987)$  experimentally studied. When plotted versus  $[\text{Ag}^+]^{-1}$  these quantities could easily be extrapolated to  $[\text{Ag}^+]^{-1} = 0$ , corresponding to  $\underline{a}_{1j} = 1$ , to give  $\underline{a}_1^*$  and hence individual  $\underline{a}_{1j}$  values.

In Fig. 3 the experimental activities  $\underline{a}_1$  determined by this procedure are compared with Temkin activities  $\underline{a}_1 = \underline{x}_1^3$ , assuming ideal mixing of  $\text{Na}^+$  with  $\text{Ag}^+$  on a fixed cation sublattice in solid  $(\text{Ag}, \text{Na})_3\text{PO}_4$ . This relation seems to be valid only for dilute solutions with  $\underline{x}_2 \leq 0.05$ .

For the equilibrium



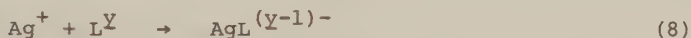
the solubility constant  $K_s$  is defined as  $K_s = [\text{Ag}^+]^3 [\text{PO}_4^{3-}] a_1$ . Due to the regrettably large scatter in solubility data and an unfavourable relation between the magnitudes of  $K_s$  and the stability constants, it was found impossible to estimate individual constants  $K_s$ ,  $\beta_{11}$  and  $\beta_{21}$  from these data. The limited solubility of alkali phosphate also checkmates any attempt to direct determination of  $K_s$  by a potentiometric technique employing the Ag(I)/Ag couple. The data were therefore treated in the following way. Concentrations of uncomplexed ion,  $[\text{Ag}^+]$  and  $[\text{PO}_4^{3-}]$ , were calculated for every experimental ( $C_{\text{Ag}}$ ;  $C_{\text{P}}$ ) couple by means of  $\beta_{11}$  and  $\beta_{21}$  from potentiometric measurements in unsaturated melts at 553 K. Then  $a_1$  values (which are rather insensitive to moderate changes in  $\beta_{11}$  and  $\beta_{21}$ ) were computed and finally  $K_s$  was calculated as an average over 24 data points.  $K_s = (7 \pm 2) \times 10^{-12} \text{ mol}^4 \text{ kg}^{-4}$  is obtained. There is no significant systematic trend in individual  $K_s$  values as  $C_{\text{P}}$  or  $C_{\text{Ag}}$  changes. This is indirectly demonstrated in Fig 4, where experimental solubilities are compared with a solubility curve calculated by means of  $K_s$ ,  $\beta_{11}$  and  $\beta_{21}$ . The complex model that describes potentiometric data from unsaturated melts thus gives a good representation of solubility data as well.

## Discussion.

The low solubilities of  $\text{Ag}_3\text{PO}_4$  and alkali phosphate make the concentration range available for emf measurements very narrow. As can be seen from Fig. 1 it would have been desirable to extend the measurements far above the concentration limit  $[\text{PO}_4^{3-}] = 8 \times 10^{-4}$

mol kg<sup>-1</sup>, which is practically impossible. As a consequence the measured  $\Delta E$  values are very small and the precision in  $\beta_{11}$  and  $\beta_{21}$  becomes rather poor, which in turn is the reason for the large uncertainty in  $\Delta H_1^O$  and  $\Delta S_1^O$ . It is obvious, however, that the stabilities of  $\text{AgPO}_4^{2-}$  and  $\text{Ag}_2\text{PO}_4^-$  are significantly higher than those of the analogous Ag(I) complexes with oxoligands of lower anionic charge in the same solvent, *viz.*  $\text{IO}_3^-$ ,  $\text{CrO}_4^{2-}$  and  $\text{MoO}_4^{2-}$ , which have previously been studied by us.

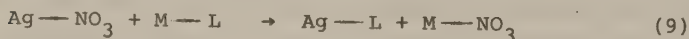
Table 2 reviews the thermodynamic parameters estimated by us for the formation of a number of 1:1 complexes of Ag(I) with oxoanions in molten equimolar (K,Na)NO<sub>3</sub> in the range 250-350°C. The crude  $\text{PO}_4^{3-}$  data have been included, since they, after all, are the most probable estimates at the present state of our knowledge. The comparison is limited to the first complexation step, schematically written as



since the stability constants  $\beta_{12}$  for the second step are as a rule impaired by wider limits of uncertainty. It is also advisable to restrict a thermodynamical comparison to process (8), since it represents the simplest possible reaction step, starting for all ligands with the same acceptor configuration, schematically written as  $\text{Ag}^+$ .

In a discussion of the magnitude of  $\Delta H_1^O$  one should first note that the comparably large exothermal value for formation of  $\text{AgNO}_2$  is probably due to the fact that Ag coordinates to nitrogen,<sup>1</sup> whereas oxygen coordination is likely to occur with the other ligands. For  $\text{IO}_3^-$ ,  $\text{CrO}_4^{2-}$ ,  $\text{MoO}_4^{2-}$  and  $\text{PO}_4^{3-}$  one may note that  $\Delta H_1^O$  is roughly proportional to the ionic charge difference between ligand and  $\text{NO}_3^-$  with a factor of about -7 kJ mol<sup>-1</sup> per negative charge unit. This value also coincides with  $\Delta H_1^O$  for the formation of  $\text{CaIO}_3^+$  in (K,Na)NO<sub>3</sub> melts<sup>13</sup> where the corresponding cationic charge difference is 1, and the observation could be taken as an indication that the magnitude of  $\Delta H_1^O$  can be explained as

mainly due to differences in coulombic hard-sphere ion-ion interaction energies. A quantitative calculation of these effects is hard to make, mainly because of the difficulty in assigning proper radii values to the polyatomic ions. If, however, an internally consistent set of radii is chosen, it would at least be possible to order the coulombic hard-sphere contributions to  $\Delta H_1^0$  for  $\text{PO}_4^{3-}$ ,  $\text{CrO}_4^{2-}$  and  $\text{MoO}_4^{2-}$ , all of tetrahedral geometry. Using the thermochemical radii of Kapustinskii<sup>14</sup> for the anions, one obtains a sequence of electrostatic energy differences for the exchange processes (charges omitted for simplicity)



which is in accordance with the trend in  $\Delta H_1^0$ , values if the exchanged alkali ion  $\text{M}^+$  is considered to be larger than  $\text{Ag}^+$ .

The experiment with  $(\text{K}, \text{Li})\text{NO}_3$  solvent described in this paper clearly showed however, that the increased affinity of  $\text{PO}_4^{3-}$  for smaller alkali metal ions observed by Smith and Alberty<sup>15</sup> in aqueous solution, is accentuated in molten alkali metal salts.  $\text{Li}^+$  competes successfully with  $\text{Ag}^+$  as coordination partner to the high charged  $\text{PO}_4^{3-}$  ions. If the same tendency to selective cationic solvation is operative for all polyvalent oxoligands, one should rather look upon the  $\text{Ag}(\text{I})$  complexation in  $(\text{K}, \text{Na})\text{NO}_3$  as a cation exchange of mainly  $\text{Na}^+$  for  $\text{Ag}^+$  in the coordination sphere of the polyvalent oxoligand. Since  $\text{Na}^+$  is smaller than  $\text{Ag}^+$ , the coulombic hard-sphere contributions would order in a sequence opposite to the one observed for  $\Delta H_1^0$

It is therefore highly probable that the  $\text{Ag} - \text{O}$  bondings have considerable covalent character, which could also be experimentally demonstrated for the  $\text{CrO}_4^{2-}$  complexes by spectrophotometry.<sup>3</sup> Duffy and Ingram recently suggested that optical basicities, as defined by them,<sup>16</sup> would measure the electron donating power of an oxoanion. Hence, one might expect some correlation between our set of  $\Delta H_1^0$  values and the basicities of the oxoanions, relating to the strengths of the  $\text{Ag} - \text{O}$  bonds. No good correlation

is found, however, but one should possibly include some solvent cations into the chemical unit for which the basicity is calculated (as proposed by Duffy for hydrogen sulphate melts<sup>17</sup>), since cationic solvation effects seem to be of importance for the polyvalent oxoanions. Such calculations would require an independent knowledge of the cationic structure around the oxoligands which is not available at present.

The data of Table 2 also demonstrate the vital importance of the entropy change for the complex stabilities. This is best seen by a comparison between  $\text{NO}_2^-$  and  $\text{IO}_3^-$ .  $\beta_{11}$  for the silver complex is about the same at 553 K, but the  $\Delta H_1^0$ - $\Delta S_1^0$  patterns are quite different,  $\text{AgNO}_2$  being enthalpy stabilized and  $\text{AgIO}_3$  entropy stabilized. For the ligands  $\text{CrO}_4^{2-}$ ,  $\text{MoO}_4^{2-}$  and  $\text{PO}_4^{3-}$  no such extreme situation is found;  $\Delta H_1^0$  and  $-\Delta S_1^0$  contribute to  $\Delta G_1^0$  by comparable amounts.

Finally one may observe that the smallest  $\Delta S_1^0$  is obtained for complexation with the divalent ions  $\text{CrO}_4^{2-}$  and  $\text{MoO}_4^{2-}$ . This could be partly due to the fact that complex anions with the same charge, -1, as the solvent  $\text{NO}_3^-$  are formed, and these anions might fit better into the melt structure than neutral or polyvalent complexes.

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Table 1. The ever-all stability constants  $\beta_{11}$  and  $\beta_{21}$  for  $\text{Ag}^+ - \text{PO}_4^{3-}$  complexes in molten 1:1 (K,Na) $\text{NO}_3$  from emf measurements. The limits of error are 95% confidence limits.  $N$  is the number of melt compositions studied at each temperature.

| $T/\text{K}$ | $\beta_{11}/\text{mol}^{-1}\text{kg}$ | $\beta_{21} \cdot 10^{-4}/\text{mol}^{-2}\text{kg}^2$ | $N$ |
|--------------|---------------------------------------|-------------------------------------------------------|-----|
| 524          | $62 \pm 23$                           | $5.6 \pm 1.1$                                         | 63  |
| 538          | $73 \pm 23$                           | $2.8 \pm 1.1$                                         | 70  |
| 553          | $78 \pm 11$                           | $2.7 \pm 0.5$                                         | 56  |
| 588          | $47 \pm 13$                           | $1.9 \pm 0.6$                                         | 71  |
| 622          | $54 \pm 13$                           | $0.6 \pm 0.6$                                         | 56  |

Table 2. Enthalpy, entropy and free energy changes for the simplified reaction  $\text{Ag}^+ + \text{L}^{\text{Y}-} \rightarrow \text{AgL}^{(\text{Y}-1)-}$  in molten equimolar (K,Na) $\text{NO}_3$ . Stated errors are one estimated standard deviation.

| $\text{L}^{\text{Y}-}$ | $\Delta H_1^{\text{O}}/\text{kJ} \cdot \text{mol}^{-1}$ | $\Delta S_1^{\text{O}}/\text{J mol}^{-1}\text{K}^{-1}$ | $\Delta G_1^{\text{O}}/\text{kJ mol}^{-1}\text{K}^{-1}$<br>at 553 K | Ref       |
|------------------------|---------------------------------------------------------|--------------------------------------------------------|---------------------------------------------------------------------|-----------|
| $\text{NO}_2^-$        | $-23 \pm 1$                                             | $-15 \pm 2$                                            | $-14.3 \pm 0.4$                                                     | 1         |
| $\text{IO}_3^-$        | $2.3 \pm 1.6$                                           | $31 \pm 3$                                             | $-14.7 \pm 0.3$                                                     | 2         |
| $\text{CrO}_4^-$       | $-6.0 \pm 1.5$                                          | $20 \pm 3$                                             | $-17.4 \pm 0.1$                                                     | 3         |
| $\text{MoO}_4^{2-}$    | $-7.5 \pm 1.6$                                          | $20 \pm 3$                                             | $-18.5 \pm 0.2$                                                     | 4         |
| $\text{PO}_4^{3-}$     | $-12.4 \pm 6.7$                                         | $33 \pm 12$                                            | $-30.9 \pm 0.7$                                                     | This work |

### Figure Legends.

Figure 1.  $\underline{C}_{\text{Ag}}/[\text{Ag}^+]$  as a function of  $[\text{PO}_4^{3-}]$  from three titrations at 553 K with different  $\underline{C}_{\text{Ag}}$ .  $\underline{C}_{\text{Ag}} = 0.64 \times 10^{-3}$  (o),  $1.20 \times 10^{-3}$  mol kg<sup>-1</sup> (□), and  $1.63 \cdot 10^{-3}$  mol kg<sup>-1</sup> (V). The graphs are calculated from the stability constants of Table 1.

Figure 2. Mole fraction  $\underline{x}_2$  of  $\text{Na}_3\text{PO}_4$  in the solid phase  $(\text{Ag},\text{Na})_3\text{PO}_4$  as a function of total phosphate concentration,  $\underline{C}_p$ , in the melt. Data from solubility measurements of  $\text{Ag}_3\text{PO}_4$  in molten 1:1 (K,Na) $\text{NO}_3$  at 553 K.

Figure 3. The activity  $\underline{a}_1$  of  $\text{Ag}_3\text{PO}_4$  in solid  $(\text{Ag},\text{Na})_3\text{PO}_4$  at 553 K as a function of the Ag(I) fraction  $\underline{x}_1$ . Experimental points from eqn. (6). The ideal Temkin activity is given by the graph.

Figure 4. Solubility curve for  $\text{Ag}_3\text{PO}_4$  in molten equimolar (K,Na) $\text{NO}_3$  at 280°C. The graph is calculated as described in the text.

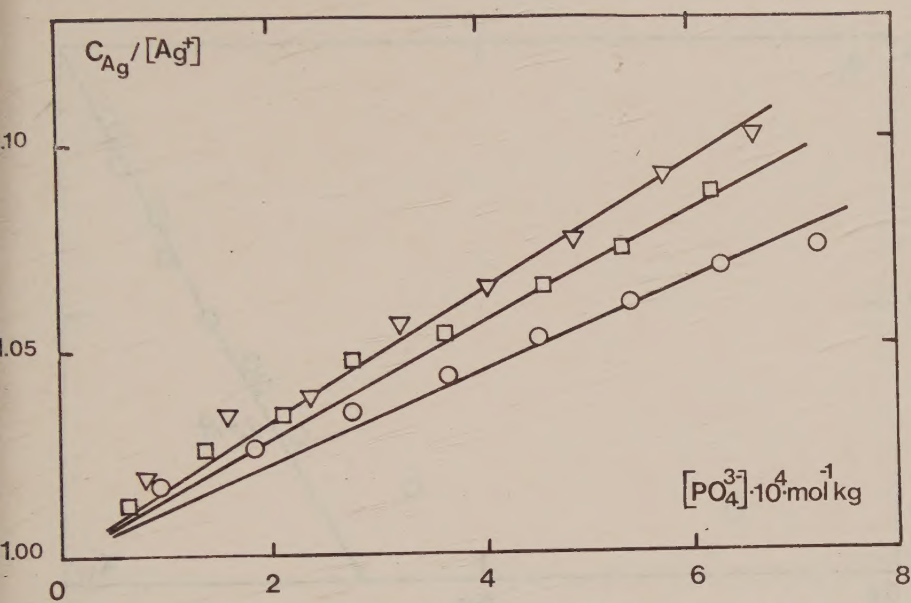


Fig. 1

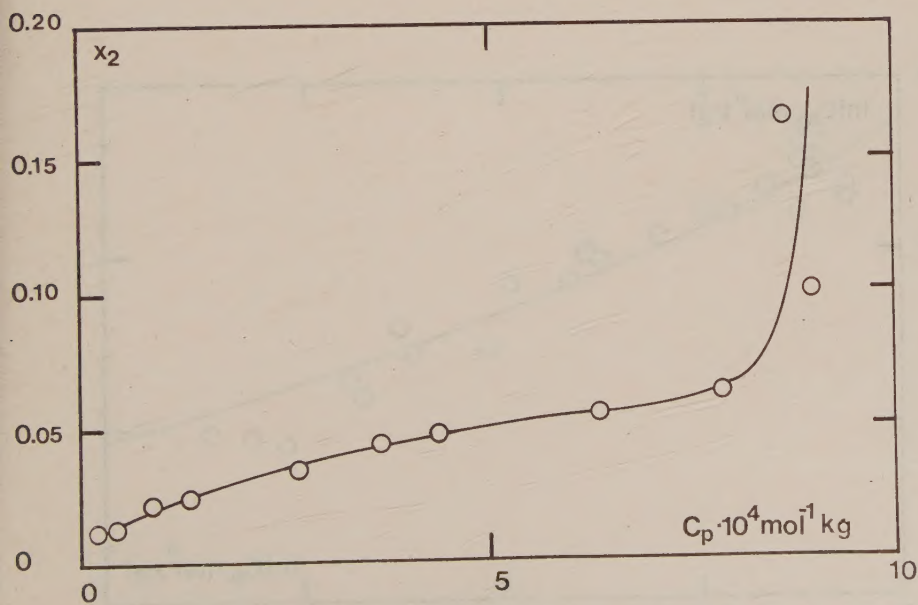


Fig. 2

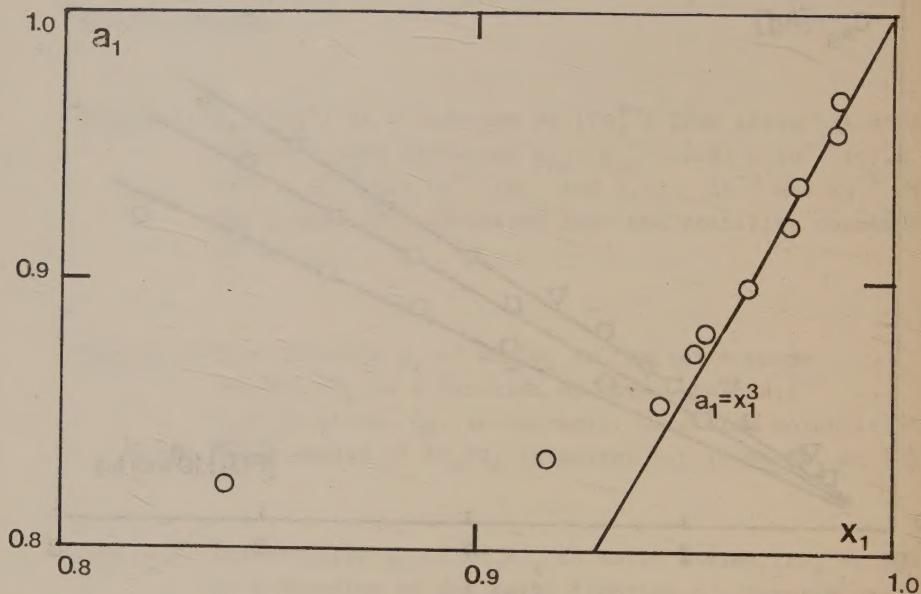


Fig. 3

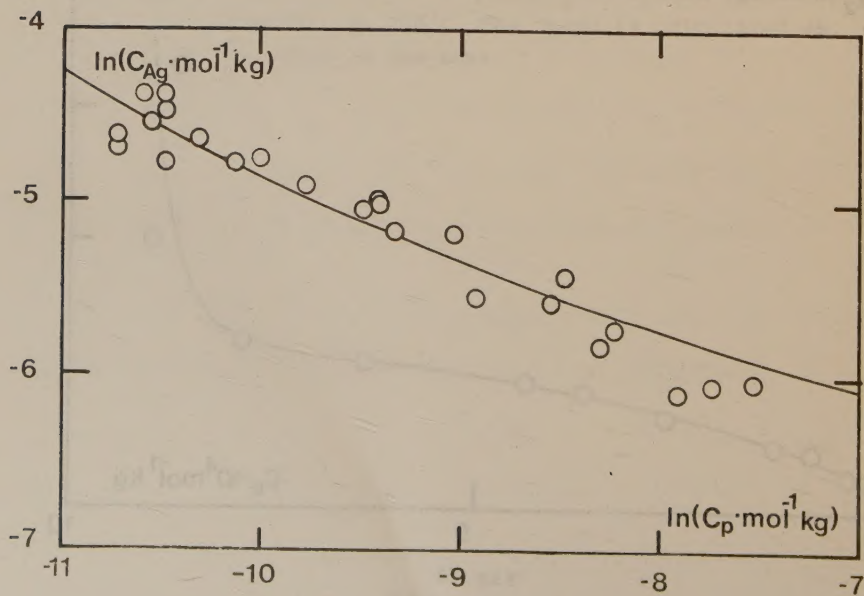


Fig. 4



